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PREFACE

This volume represents a continuing effort to cover comprehensively the unclassified information on explosives and related subjects in the same manner and format as in previous volumes. The reader is urged to obtain the previous volumes and to read both the PREFACE and INTRODUCTION in Volume 1 in order to understand the authors' way of presenting the subject matter.

In preparation for and during the writing of this Encyclopedia, the authors have consulted freely with and have had the cooperation of many individuals who contributed their expert knowledge and advice. This fact is acknowledged throughout the text at the end of the subject item. A listing of many others who have helped in various ways would be impractical.

Drs J. Roth, J. Brown, A.P. Hardt and Mr T.Q. Ciccone of the private sector, Dr C.H. McDonnell of the Naval Ordnance Station, Indian Head, Md, as well as Dr S. Bulusu and Messrs S. Helf, H.L. Herman, J. Hendrickson and D.J. Veal of the Energetics Materials Division, LCWSL, ARADCOM, Dover, NJ, all contributed significantly in the literature searching and writing of many of the articles in this volume. Others who contributed to the manuscript, by invitation, are indicated at the end of the articles.

Dr Raymond F. Walker, Energetics Materials Division Chief, provided financial support and encouragement to continue this work, as did Mr Edward J. Kolp of Headquarters, US Army Materiel Development and Readiness Command (DARCOM). Further financial support was received from the sale of copies to non-government agencies and individuals by the National Technical Information Service, US Department of Commerce, Springfield, Va 22161.

Although considerable effort has been made to present this information as accurately as possible, mistakes and errors in transcription and translation do occur. Therefore, the authors encourage the readers to consult original sources, when possible, and to feel free to point out errors and omissions of important works so that corrections and additions can be listed in the next volume. The interpretations of data and opinions expressed are often those of the authors and are not necessarily those nor the responsibility of officials of ARADCOM or the Department of the Army.

This report has been prepared for information purposes only and neither ARADCOM nor the Department of the Army shall be responsible for any events or decisions arising from the use of any information contained herein.

It will be noted that a change in editors has taken place since the publication of Volume 7 in 1975, this change being the first since the inception of the Encyclopedia program in 1958. It was necessitated by the death of Dr Basil T. Fedoroff in December 1976 (see obituary which follows), and the retirement of Mr Oliver E. Sheffield in October 1975 after some 34 years of Federal service, with incumbency at Picatinny Arsenal since January 1943. He authored or co-authored over 40 Picatinny Arsenal Technical Reports and AMC Manuals on explosives, pyrotechnics and propellants. Sheffield is best known as co-editor of this Encyclopedia, with which he was associated since 1958.

This change in editorial leadership has resulted, perhaps inevitably, in a change in editorial policy which is reflected in the contents of Volume 8. There has been a marked de-emphasis on the inclusion of organic "parent compounds" followed by an exhaustive and voluminous cataloging of azide, azido, azo, diazido, diazonium, diazo, nitro, dinitro, polynitro, nitramine, nitrate (esters and salts), dinitrate, polynitrate, nitroso, polynitroso, chlorate, perchlorate, peroxide, picrate, etc, derivatives—regardless of whether any of these derivatives exhibit documented explosive or energetic properties. Only those materials having such properties have been included in this volume.

There has also been a distinct effort made not to include subject areas which are not specifically pertinent to the subject of energetic materials.

In conclusion, I wish to acknowledge with gratitude the continual support and encouragement of Samuel Helf, without whose efforts in behalf of the Encyclopedia of Explosives program, the publication of this volume would not have been possible.

Seymour M. Kaye
Dover, New Jersey
March 1978
IN MEMORIAM

BASIL T. FEDOROFF
(1891–1976)

Dr. Basil T. Fedoroff, scientist and engineer, who worked at Picatinny Arsenal from 1946–1961 and served as an Arsenal consultant from 1961–1975, died in Miami, Florida on 29 December 1976 at the age of 85. Dr. Fedoroff, who was best known as the Chief Editor of the “Encyclopedia of Explosives and Related Items”, Volumes 1 to 7 (1960–1975), was born in Merv, Russia on 8 January 1891. He graduated from the Imperial Tomsk Institute of Technology as a chemical engineer in 1914, and earned his doctorate in the same field from the University of Paris, Sorbonne in 1940.

After graduating from Tomsk, he served in the Imperial Russian Navy and the French Foreign Legion. He came to the United States by way of Canada in the early 1920's and obtained his citizenship in 1927. He enrolled at Sorbonne in 1931 and returned to this country after obtaining his doctorate.

From 1941 until he came to Picatinny Arsenal, Dr. Fedoroff worked in private industry in the field of explosives and propellants. He joined the staff of the Picatinny Arsenal Technical Division as a research chemist in 1946, and remained until his retirement in 1961. In addition to the Encyclopedia, his major publications include “A Manual for Explosives Laboratories”, 4 volumes (1942–46) in collaboration with C. D. Clift; “Dictionary of Russian Ammunition and Weapons” (1955); and “Dictionary of Explosives, Ammunition and Weapons (German Section)” (1958).

Dr. Fedoroff was a unique repository of historical facts, as well as an internationally recognized expert in energetic materials.
Errata in Volume 6

p E264-R, third paragraph  The US Military Specification for Ethylene Glycol Dinitrate (EGDN) is MIL-E-48225 (1973)

p F135-R, second paragraph  "reducing" instead of "oxidizing" materials

p F221-R, second paragraph  "0.12 cal/g°C" instead of "1.1 cal/g°C"

Errata in Volume 7

Addendum III  Empirical formula should read C_{10}H_{10}H_8N_8O_{17}

Addendum IV  Ethanol group on carbon 3 of second structural formula should read C_2H_4OH

p H66-L, first paragraph  Should be placed on lower part of p H67-L following "with substantial cost savings"

p H67-L, first 3 paragraphs ending with "with substantial cost savings"  Should follow "In addition" at bottom of p H65-R

p H67-L from "produced at Rocky Hill"  Should follow last sentence at bottom of p H66-R

p H237-R, second and third paragraphs  "3,5-Dinitro-2-Hydroxybenzoic Acid" instead of "3,5-Dinitro-4-Hydroxybenzoic Acid"

p H226 title  "Peroxides" instead of "Peroxides"

p L20-L, third paragraph  "Because" instead of "Because"

p L28-L, last paragraph  "interesting" instead of "itneresting"

p L29-R, last paragraph  "optical" instead of "optional"

p L43-R, fifth paragraph  (Ref 29, p 344) instead of (Ref 30, p 344)
IV

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VOL 4, pp XLVII to L; VOL 5, p XIII; and VOL 7, p X


Propints & Expls (Vol, No, Year & Page) Propellants and Explosives, Verlag Chemie International Inc, NY (Vol 1, No 1 published April 1976)

SUPPLEMENT TO THE
LIST OF BOOKS ON EXPLOSIVES, PROPELLANTS, PYROTECHNICS AND ORDNANCE ITEMS
GIVEN IN VOL 1, p A676; VOL 2, pp C215 to C216; VOL 3, pp XIV to XV; VOL 4, pp L1 to LV;
VOL 5, pp XIV to XV; VOL 6, p X; and VOL 7, pp XI to XII

Materiel Command, 5001 Eisenhower Ave, Alexandria, Va 22333 (Dec 1975)

Materiel Command, 5001 Eisenhower Ave, Alexandria, Va 22333 (Sept 1975)

Boston, Mass 02210 (1975)


Anon, "Incendiary Weapons", Stockholm International Peace Research Institute, MIT Press,
Cambridge, Mass (1975)

Anon, "Toxic and Hazardous Industrial Chemicals Safety Manual", The International Technical
Information Institute, Tokyo (1975)


P.H.C. Hayward, "Jane's Dictionary of Military Terms", MacDonald and Jane's, London (1975)

L.F. Albright and C. Hanson, Edits, "Industrial and Laboratory Nitrations", ACS Symposium Series
22, American Chemical Society, Washington, DC (1976)

Anon, "Dictionary of Basic Military Terms — A Soviet View", US Govt Printing Office, Washington,
DC (1976) (Stock No 008-070-00360-1)


Plenum Press, NY (1977)

M1 Thickener. A standard thickener for prepping an incendiary known as Napalm. It is a mixed Al soap in which about 50% of the org acids are derived from coconut oil, 25% from naphthenic acids and 25% from oleic acid. When stirred into gasoline at a temp range from 16–29°C, M1 swells until the entire vol of gasoline becomes a more or less homogeneous gel.

M2 Thickener. A standard (for US Air Force) incendiary oil thickener. It is an intimate mix of 95% M1 Thickener and 5% devolutilized silica aerogel or other approved antiagglomerate. M2 Thickener is an improvement over M1 for use in fire bombs, not only because of free flowing and faster setting characteristics, but also because the thickener itself and gel formed are more stable.

M4 Thickener. A standard incendiary oil thickener. It is a diacid Al soap of isoctanoic acids derived from isoctyl alc or isoctyl aldehyde obt from the oxidn of petroleum. It contains 2% Santocel C or Attaclay SF which serves as an antiagglomerant. About 1/2 the amt of M4 and about 1/10 mixing time is reqd for M4 Thickener as compared to M1 for thickened fuels of comparable consistency. Fuels prepd with M4 are superior in flame throwing performance with respect to range, burning and target effects, as compared with fuels prepd with other thickeners.

Ref: Anon, “Military Chemistry and Chemical Agents”, TM 3-215/AFM 365-7 (Dec 1963), 41

Macaroni Press. A hydraulic press with a perforated false bottom. A so-called preliminary block is placed between the piston of the press and the bottom. This block consists of NC, previously colloided in a kneading machine with solvents such as eth-al, acet, etc, blended with other ingredients such as diphenylamine, dinitrotoluene, etc, and pressed at about 3500 psi in a preliminary blocking press into a compact mass. The block is subjected to a press of 3000–3500psi in the macaroni press and squeezed sequentially thru one 12 mesh steel wire screen, two 24 mesh screens, one 36 mesh screen, and then thru the perforations of a heavy brass plate, from which it emerges in worm like strands resembling macaroni. The strands drop directly into the cylinder of a final blocking press, where it is compressed into a compact cylindrical block of the proper size to fit a graining press. The purpose of the macaroni press is to achieve more thorough

4C₇H₈(NO₂)₃ + 7Pb(NO₃)₂ =
28CO₂ + 10H₂O + 13N₂ + 7Pb
(Refs 1 & 2). Later Belg comps contd TNT 30–50 and Pb nitrate 50–70% (Refs 1, 2, 3 & 4). Barnett (Ref 4) gives the following data for 30/70 Macarite: deton vel 4600m/sec at d 1.65g/cc, 4700m/sec at d 2.75g/cc and 4860 m/sec at d 2.89g/cc, vs 7100m/sec for PA at d 1.60g/cc; briance as detd by crushing the Cu cylinder of Kast's briance meter 2.52mm at d 2.65g/cc and 2.86mm at d 2.75g/cc, vs 3.88mm at d 1.60g/cc for PA. Marshall (Ref 2, p 449) compared some of its expl properties with PA and TNT and concluded that, although its deton vel is considerably less than that of PA and TNT, the briance and relative energy "f" of Macarite are slightly higher. Macarite was used in Belg for a considerable period of time, primarily because of its insensitivity to shock, non-hygroscopicity, non-corrosive effect on metals, and safety in manuf, storage and transportation.

Refs: 1) E. Bravetta, SS 7 (1913), 124
2) Marshall 2 (1917), 449 & 557
3) Colver (1918), 247
4) Barnett (1919), 185 & 193
5) A. Pérez Ara (1945), 505

Macarites. Expls introduced in 1891 by J. de Macar of Belg, with the primary objective of replacing PA (Lyddite or Melinite) for filling HE shells, torpedoes, etc. The original Macarite contd TNT 28.1 and Pb nitrate 71.9% at d 2.7–2.8g/cc. Its deton reaction showed complete combn to CO₂, H₂O and Pb:
blending of the ingredients of smokeless powder than could be achieved in the kneading machine and to effect more thorough gelatinization of the NC

Ref: Davis (1943), 302

MacEvoy. Proposed to use primers containing metallic Na and W in separate compartments. A hot flame was produced on the contact of the ingredients

Ref: Daniel (1902), 414

MacGavin Explosive. Prepared by saturating sawdust with a solution of K picrate, drying the resulting powder, and mixing it with K or Na nitrate and S

Ref: Daniel (1902), 414

Mach Number. (abbr M). The ratio of the velocity of a body to that of sound in the medium being considered. Thus, at sea level, in air at the US Standard Atm, a body moving at a Mach number of one (M=1) would have a velocity of 1116.2 ft/sec; the speed of sound in air under these conditions. The term is frequently shortened to mach or Mach. Named for Ernst Mach, 1838-1916, Austrian physicist

Ref: OrdTechTenn (1962), 184

Mach Stem. A shock wave or front formed above the surface of the earth by the fusion of direct and reflected shock waves resulting from an airburst. Also called mach wave and mach front

Ref: OrdTechTenn (1962), 184

Machine Gun. Automatic weapons which fire small arms ammunition. They are heavier than automatic rifles and are usually provided with a fixed mount, such as a tripod, or wheels and a trail. These sustain the force of recoil and provide the means by which the gun may be positioned in the direction of fire. Machine guns utilize the discharging gas, or mechanical recoil of the gun to load, eject the cartridge, lock, and unlock the breech. They are fed from either a belt, clip, or magazine, and are cooled by either a jacket around the barrel, or by radiation from metal fins. The machine gun provides a sustained-fire weapon that can be used effectively against personnel and lightly armored vehicles, or for area fire to harass an enemy when he cannot be precisely located


MacKintosh Propellants. Prepared by mixing fine BlkPdr with a rubber soln, spreading the powder on fabric, drying & cutting to desired grain size. K chlorate was added to increase burning rate, bran or other materials to decrease it. Patented in 1857

Ref: Daniel (1902), 415


Magnesium. Mg, at wt 24.312, at no 12, valence 2. Isotopes: 24 (77.4%), 25 (11.5%) & 26 (11.1%). Physical properties of 99.9% pure Mg are given in the following table (Ref 19, p 679).

Mg is very abundant in nature, occurring in substantial amounts in many rock-forming minerals such as dolomite, magnesite, olivine, and serpentine. In addition, it is also found in seawater, subterranean brines, and salt beds. It has been estimated that Mg constitutes 2.5% of the earth's crust, being exceeded only by Al and Fe.

Mg is insol in cold w; sl sol in hot w, with which it reacts; sol in mineral acids, conc HF and Amm salts; insol in chromates & alkali.

In 1808, Sir Humphry Davy reported the production of Mg in the form of an amalgam by electrolytic reduction of its oxide using a Hg cathode. In 1828, the Fr scientist A. Bussy fused Mg chloride with metallic K and became the first to produce free metallic Mg. Michael Faraday, in 1833, was the first to produce free metallic Mg by electrolysis, using Mg chloride. For many years, however, the metal remained a laboratory curiosity. In 1886, manuf of Mg was undertaken on a production scale in Ger, using electrolysis of fused Mg chloride. Until 1915, Ger remained the sole producer of Mg. However, when a scarcity of Mg arose in the USA as a result of the Brit blockade of Ger in 1915, and the price of Mg soared from $1.65 to $5.00 per lb, three producers initiated operations and thus started a Mg industry in the USA. Subsequently, additional companies attempted production of Mg, but by 1920 only two producers remained — The Dow Chemical Co (one of the original three producers) and the American Magnesium Corp. In 1927, the latter ceased production, and Dow continued to be the sole domestic producer until 1941. The source of Mg chloride was brine pumped from deep wells. In 1941, Dow put a plant into operation at Freeport, Texas, obtaining Mg chloride from seawater. Also in 1941, Permanente Metals Corp began to produce Mg at Permanente, Calif, using the carbothermic process invented by Dr. F.J. Hunsig, an Austrian scientist. In addition to these new privately owned plants, Government plants were constructed, and by 1943 there were thirteen more plants in operation under the management of eleven different companies.

Six of the plants were electrolytic, of which two utilized seawater and three used dolomite. The remaining plant used calcined magnesite, which was chlorinated to anhydrous Mg chloride in an electric furnace by a method originated in Ger. The other Government plants were thermal reduction operations which utilized the ferrosilicon process.

There are currently three producers of Mg in the USA. The Dow Chemical Co is by far the largest producer, all of it by the electrolytic process. Alcanet Division of Calumet & Hecla, Inc., produces Mg from dolomite by the ferrosilicon process in their plant at Selma, Alabama. Titanium Metals Corp also produces Mg as a by-product of their Ti production (Ref 19, p 664).

The electrolysis of Mg chloride to yield chlorine and metallic Mg is the basis of the electrolytic process. Sea w is pumped into large settling tanks where it is mixed with lime obtained by roasting oyster shells dredged from the ocean bottom. The lime converts the Mg into insol Mg hydroxide which is filtered out. This hydroxide is then treated with HCl, obtained from chlorine by reaction with natural gas, to produce Mg chloride soln. The w is evapd, and the dry Mg chloride is fed to the electrolytic cells which separate it into metallic Mg and chlorine, the Mg being poured into ingots. The ferrosilicon process, although first originated experimentally in Ger, was developed commercially during WWII in Canada. Ferrosilicon, an alloy of Si and Fe, is mixed with calcined dolomite ore and pressed into small briquets. These are charged into a steel retort, put under vacuum, and heated to about 2200°F. The Si reduces the Mg oxide (formed by calcining of the dolomite) to form a vapor of metallic Mg which condenses in the cool end of the retort. The Mg is removed in the form of crystals, which are subsequently melted and cast into ingots (Refs 3, 18 & 25)
<table>
<thead>
<tr>
<th>Property</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>At vol, cm³/g-atom</td>
<td>14.0</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>close-packed hexagonal</td>
</tr>
<tr>
<td>Lattice parameters, Å</td>
<td></td>
</tr>
<tr>
<td>Axial ratio, $c/a$</td>
<td>1.624</td>
</tr>
<tr>
<td>Modulus of elasticity, kg/mm²</td>
<td>4570</td>
</tr>
<tr>
<td>of rigidity, kg/mm²</td>
<td>1700</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.35</td>
</tr>
<tr>
<td>Density, g/cm³, at</td>
<td></td>
</tr>
<tr>
<td>20°</td>
<td>1.74</td>
</tr>
<tr>
<td>650°C (solid)</td>
<td>1.64</td>
</tr>
<tr>
<td>650°C (liquid)</td>
<td>1.57</td>
</tr>
<tr>
<td>700°C</td>
<td>1.54</td>
</tr>
<tr>
<td>Volume contraction, 650°C (liquid) to 650°C (solid)</td>
<td>4.2%</td>
</tr>
<tr>
<td>Linear contraction, 650°C (solid) to 20°C (solid)</td>
<td>1.8%</td>
</tr>
<tr>
<td>Electrical resistivity, $\mu\Omega$-cm, at</td>
<td></td>
</tr>
<tr>
<td>20°</td>
<td>4.46</td>
</tr>
<tr>
<td>300°</td>
<td>9.5</td>
</tr>
<tr>
<td>600°</td>
<td>17.0</td>
</tr>
<tr>
<td>650°C (liq)</td>
<td>28.0</td>
</tr>
<tr>
<td>900°</td>
<td>28.0</td>
</tr>
<tr>
<td>Temp coeff, at 20°C, $\mu\Omega$-cm/°C</td>
<td>0.017</td>
</tr>
<tr>
<td>Electrical conductivity, at 20°C, annealed copper (standard)</td>
<td></td>
</tr>
<tr>
<td>mass %</td>
<td>198.0</td>
</tr>
<tr>
<td>vol %</td>
<td>38.6</td>
</tr>
<tr>
<td>mp, °</td>
<td>650</td>
</tr>
<tr>
<td>bp, °</td>
<td>1110 ± 10</td>
</tr>
<tr>
<td>Critical temp, calc</td>
<td>1867</td>
</tr>
<tr>
<td>Flame temp, theoret °C</td>
<td>4850</td>
</tr>
<tr>
<td>Coeff of expansion</td>
<td></td>
</tr>
<tr>
<td>coeff of thermal expansion, in/(in)(°C), at</td>
<td></td>
</tr>
<tr>
<td>20–100°C</td>
<td>0.0000261</td>
</tr>
<tr>
<td>20–200°C</td>
<td>0.0000271</td>
</tr>
<tr>
<td>20–300°C</td>
<td>0.0000280</td>
</tr>
<tr>
<td>20–400°C</td>
<td>0.0000290</td>
</tr>
<tr>
<td>20–500°C</td>
<td>0.0000299</td>
</tr>
<tr>
<td>Specific heat, cal/(g)(°C), at</td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td>0.245</td>
</tr>
<tr>
<td>300°</td>
<td>0.275</td>
</tr>
<tr>
<td>650° (solid)</td>
<td>0.325</td>
</tr>
<tr>
<td>650° (liq)</td>
<td>0.316</td>
</tr>
<tr>
<td>Thermal conductivity, cal/(sec)(cm²)(°C/cm), at 20°C</td>
<td>0.37</td>
</tr>
<tr>
<td>Thermal diffusivity, cm²/sec, at 20°C</td>
<td>0.87</td>
</tr>
<tr>
<td>Heat of combustion, cal/g-mole</td>
<td>145,000</td>
</tr>
<tr>
<td>Latent heat of fusion, cal/g</td>
<td>88 ± 2</td>
</tr>
<tr>
<td>Latent heat of evaporation, cal/g</td>
<td>1260 ± 30</td>
</tr>
<tr>
<td>Heat of reaction with oxygen, at 2900K, 1 atm magnesium</td>
<td></td>
</tr>
<tr>
<td>Btu/lb metal</td>
<td>8,180</td>
</tr>
<tr>
<td>Btu/lb O₂</td>
<td>12,430</td>
</tr>
<tr>
<td>Thermal neutron, absorption cross section barn/atom (cm²/cm³)</td>
<td>0.059 (0.00254)</td>
</tr>
</tbody>
</table>
Although Mg is generally considered nontoxic, the inhalation of fumes of freshly sublimed Mg oxide may cause metal fume fever. There is no evidence that Mg produces true systemic poisoning. Particles of metallic Mg or Mg alloy which perforate the skin or gain entry thru cuts and scratches may produce a severe local lesion characterized by the evolution of gas and acute inflammatory reaction, frequently with necrosis. The condition has been called a "chemical gas gangrene". Gaseous blebs may develop within 24 hrs of the injury. The lesion is very slow to heal (Ref 23).

Mg is a dangerous fire hazard, in the form of dust or flakes, when exposed to flame, or by violent chemical reaction with oxidizing agents. In solid form, Mg is difficult to ignite because heat is conducted rapidly away from the source of ignition; it must be heated above its mp before it will burn. However, in finely divided form it may be ignited by a spark or the flame of a match. Mg fires do not flare up violently unless there is moisture present. Therefore, it must be kept away from w, moisture, etc. It may be ignited by a spark, match flame, or even spontaneously when the Mg is finely divided and damp, particularly with w-oil emulsion. Also, Mg reacts with moisture, acids, etc to evolve H₂ which is a highly dangerous fire and explosion hazard (Ref 23).

Mg ribbon and fine Mg shavings can be ignited at air temps of about 950°F (Ref 26). Oxides of Be, Cd, Hg, Mo and Zn can react explosively with Mg when heated (Ref 8). Mg reacts with incandescence when heated with the cyanides of Cd, Co, Cu, Pb, Ni or Zn or with Ca carbide (Ref 9). It is spontaneously flammable when exposed to moist chlorine (Ref 10), and on contact with chloriform, methyl chloride (or mixts of both), an expln occurs (Ref 4). Mg also reacts violently with chlorinated hydrocarbons, nitrogen tetroxide and Al chloride (Ref 14). The reduction of heated cupric oxide by admixed Mg is accompanied by incandescence and an expln (Ref 7). Mg exposed to moist fluoride is spontaneously flammable (Ref 11). When a mixt of Mg and Ca carbonate is heated in a current of hydrogen, a violent expln occurs (Ref 12). When Mo trioxide is heated with molten Mg, a violent detonation occurs (Ref 1). Liq oxygen (LOX) gives a detonable mixt when combined with powdered Mg (Ref 15), as do phosphates (Ref 16). An expln occurred during heating of a mixt of K chloride and Mg (Ref 2), and powdered Mg plus K or Na perchlorates form friction-sensitive expl mixts (Ref 24). Eltern (Ref 22) reports that a mixt of Ag nitrate and Mg will burst into flame on moistening. The w causes electrochemical exchange between the Mg and the Ag ion. The heat of reaction of this exchange provokes the pyrochemical effect. Na peroxide oxidizes Mg powd with incandescence (Ref 5). The mixt explodes when heated to redness. When the mixt is exposed to moist air, spontaneous combustion occurs. When carbon dioxide gas is passed over a mixt of powd Mg and Na peroxide, the mixt explodes (Ref 6). Stannic oxide, heated with Mg, explodes (Ref 13). A mixt of sulfates and Mg may cause an expln (Ref 17). It has been detd experimentally that a mixt of Mg powd with trichloroethylene or carbon tetrachloride will flash or spark under light impact (Ref 21). Mg alloy powders contg more than 50% Mg readily ignite in air (Ref 20).


In the construction or assembling of certain machinery or equipment, Mg or one of its alloys having similar properties may have been used for only a few of the component parts, and where finished or painted products are being stored or handled, it may be difficult to determine which contains Mg. Investigation has shown that Ag nitrate, vinegar or acetic acid can be used to distinguish between parts composed of Mg and those composed of Al. The portion of metal to be tested is first cleaned of grease, dirt, oxide, etc, by abrading with sandpaper or steel wool. After the test area has been prep, a drop of the test soln is placed on it. (a) Ag nitrate test. The test soln is prep by dissolving about 5g of Ag nitrate in one liter of distd w. A black coloration is immediately produced on Mg or Mg alloy, the coloration being essentially reduced Ag. No coloration is noted on Al or its alloys, or most other metals. Zn and Cd will show a similar black coloration, but are much heavier (b) Vinegar or acetic acid test: Ordinary vinegar or a weak soln of acet ac will give a bubbling reaction in contact with Mg, while other common metals are not affected (Ref 5)

The requirements for the US Armed Forces are detailed in the Mil Spec listed as Ref 3, which covers powdered Mg suitable for use in ammo. It states that Mg powder shall be furnished in the following types, grades, and granulations:

Type: Type I (flaked and/or chip), Grade A (96% min Mg content), Grade B (86% min Mg content); Type II (oblong chip with rounded edges), 96% min Mg content; & Type III (atomized), 98% min Mg content

Granulation:

<table>
<thead>
<tr>
<th>Granulation</th>
<th>No.</th>
<th>Nominal US Standard Sieve Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>40 to 80</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>40 to 80 (alternate)</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>50 to 100</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>50 to 100 (Army)</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>50 to 120</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>80 to 120</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>120 to 200</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>140</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>80 to 200</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>120 to 200 (Army)</td>
</tr>
<tr>
<td>13</td>
<td>13</td>
<td>20 to 50</td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>50 to 100</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>100 to 200</td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>200 to 325</td>
</tr>
<tr>
<td>17</td>
<td>17</td>
<td>50 to 100</td>
</tr>
<tr>
<td>18</td>
<td>18</td>
<td>30 to 50</td>
</tr>
</tbody>
</table>

A detailed breakdown is given in Table II of the Spec for the min & max weight percentages allowable for retention on and passage thru specific sieves.

Material requirements are as follows:

Type I (Grade A), types II and III shall be manufd from primary Mg metal contg not less than 99.80% metallic Mg. Mica fillers or other adulterants shall not be used and “bag house dust” shall not be included in the Mg powder offered for acceptance.

Type I (Grade B) shall be manufd from Mg metal of such purity that the product meets the requirements of this Spec. Mica fillers or other adulterants shall not be used and “bag house dust” shall not be included in the Mg powder offered for acceptance.
Form requirements are as follows:
*Type I* Mg powder shall consist of shavings, turnings, flakes, plates or any combination of these which meets the granulation requirement. *Type II* Mg powder shall consist of oblong chip-like particles with rounded edges. *Type III* Mg powder shall consist of granular or spheroidal particles.

**Chemical Composition:** Mg powder shall conform to the requirements shown in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grade A</td>
<td>Grade B</td>
<td></td>
</tr>
<tr>
<td>Material volatile at 105° (max)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Oil and grease (max)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Carbides (max)</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Material insoluble in sulfuric acid (max)</td>
<td>0.15</td>
<td>—</td>
<td>0.15</td>
</tr>
<tr>
<td>Metallic iron (max)</td>
<td>0.05</td>
<td>—</td>
<td>0.05</td>
</tr>
<tr>
<td>Total iron as FeO3 (max)</td>
<td>0.25</td>
<td>—</td>
<td>0.25</td>
</tr>
<tr>
<td>Aluminum as Al (max)</td>
<td>—</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>Free metallic magnesium (min)</td>
<td>96</td>
<td>—</td>
<td>96</td>
</tr>
<tr>
<td>Aluminum plus free metallic magnesium (min)</td>
<td>—</td>
<td>96</td>
<td>—</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Granulation No.</th>
<th>Density in grams per milliliter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>1</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>0.65</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
</tr>
<tr>
<td>4</td>
<td>0.625</td>
</tr>
<tr>
<td>51</td>
<td>—</td>
</tr>
<tr>
<td>61</td>
<td>—</td>
</tr>
<tr>
<td>71</td>
<td>—</td>
</tr>
<tr>
<td>81</td>
<td>—</td>
</tr>
<tr>
<td>91</td>
<td>—</td>
</tr>
<tr>
<td>101</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>—</td>
</tr>
<tr>
<td>13</td>
<td>—</td>
</tr>
<tr>
<td>14</td>
<td>0.75</td>
</tr>
<tr>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>—</td>
</tr>
<tr>
<td>181</td>
<td>—</td>
</tr>
</tbody>
</table>

*Apparent Density:* Determined using a Scott Volumeter, with the following max & min requirements for each granulation:

<table>
<thead>
<tr>
<th>Granulation No.</th>
<th>Density in grams per milliliter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>1</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>0.65</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
</tr>
<tr>
<td>4</td>
<td>0.625</td>
</tr>
<tr>
<td>51</td>
<td>—</td>
</tr>
<tr>
<td>61</td>
<td>—</td>
</tr>
<tr>
<td>71</td>
<td>—</td>
</tr>
<tr>
<td>81</td>
<td>—</td>
</tr>
<tr>
<td>91</td>
<td>—</td>
</tr>
<tr>
<td>101</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>—</td>
</tr>
<tr>
<td>13</td>
<td>—</td>
</tr>
<tr>
<td>14</td>
<td>0.75</td>
</tr>
<tr>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>—</td>
</tr>
<tr>
<td>17</td>
<td>—</td>
</tr>
<tr>
<td>181</td>
<td>—</td>
</tr>
</tbody>
</table>

1 No determination required.
When Mg is alloyed with Al, for use in some incendiary, tracer and photoflash compus, the requirements of the US Armed Forces are given in the Mil Spec entitled, "Magnesium-Aluminum Alloy, Powdered" (Ref 1). It covers two types of Mg-Al alloy, Type A (50/50), and Type B (65/35).

Material requirements are as follows: Primary Al shall be used in the manuf of Type A alloy powder, while primary or secondary Al may be used for Type B alloy powder. Type A powder shall be granular and shall contain no slivers, chips, or machine turnings.

Chemical Composition: Mg-Al alloy powder shall conform to the composition requirements shown in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Type A</th>
<th>Type B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>50.0 ± 2.0</td>
<td>65.0 ± 2.0</td>
</tr>
<tr>
<td>Aluminum</td>
<td>50.0 ± 2.0</td>
<td>35.0 ± 2.0</td>
</tr>
<tr>
<td>Total magnesium and</td>
<td>98.0</td>
<td>98.0</td>
</tr>
<tr>
<td>aluminum (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxides as Al₂O₃ (max)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Iron as Fe (max)</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Silicon as Si (max)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Other metals (max)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Zinc as Zn (max)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Grease and fats (max)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Moisture (max)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Grit (max)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Granulation: Mg-Al alloy powder shall conform to the requirements in the following table using US Standard sieves:

<table>
<thead>
<tr>
<th>Through Sieve No.</th>
<th>Type A</th>
<th>Type B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percent</td>
<td>Percent</td>
</tr>
<tr>
<td>100</td>
<td>99.5</td>
<td>90</td>
</tr>
<tr>
<td>120</td>
<td>98</td>
<td>80</td>
</tr>
<tr>
<td>230</td>
<td>45</td>
<td>65</td>
</tr>
</tbody>
</table>

Apparent Density (Type A powder only): The apparent density of Type A powder shall not be less than 0.800 g/cc when detd using a Scott Volumeter.

Written by: S.M. KAYE


Magnesium Azide. See under Azides.

Magnesium Carbonate (Magnesia Alba), MgCO₃, mw 84.32, white prl, mp 350°, dec, 2.958 g/cc, RI 1.515 at 20°; v sl sol in w (0.0106g/100g w), insol in acet & NH₃; sol in acids & aq CO₂. Can be prep'd by boiling aq solns of Mg sulfate and Na carbonate in equimol quants, then filtering and drying the ppt. Used in 0.5 to 1.0% concn as an antacid in such coml exps as Fr Forcites (Ref 3, p 328), Belg gelatin dynamites (Ref 2, p 329) and Oaklite No 1 (Ref 3, p 402). In older Hercules exps (Poudres Hercule) it was used in 10–20% concn as an absorbent for NG. Following are some examples: a) NG 75, Mg carbonate 20.85, K nitrate 2.10, K chloride 1.05 & sugar 1.00%; b) NG 40, Mg carbonate 10, K nitrate 31, K chloride 3.34, sugar 15.66%

Magnesium Chlorate. See under Chlorates

Magnesium Cresylate. See under Cresylates

Magnesium Nitrate. See under Nitrates

Magnesium Oxide. (Magnesia), MgO, mw 40.32, colorless cubic crystals, mp 2800°, bp 3000°, d 3.58g/cc, nearly insol in w (0.00062g/100g w, 0.0086g at 30°), insol in alc, sol in acids & NH₄ salts. May be prepd either as a light, fluffy amor pdr by calcining Mg carbonate or as a heavy pdr by calcining basic Mg carbonate. Used in the prepn of Mg stypnate, a starting material for the manuf of Pb stypnate. Has been used as an antacid ingredient in some Dynamites, and in Ger smokeless pdrs during WWII as an extrusion facilitator. Following are some examples of Ger pdrs: a) flake pdr for howitzers: NC (13% N) 38.03, DEGDN 31.12, NG 30.00, akardite 0.50, graphite 0.10 & MgO 0.25% (Ref 3, p 85); b) tubular pdr for cannon: NC (12% N) 67.65, DEGDN 29.00, centralite 3.00, graphite 0.10 & MgO 0.25% (Ref 3, p 86); c) rocket pdr: NC (12.60% N) 59.03, DEGDN 34.82, hydrocellulose 3.00, ethylphenylurethane 1.90, vaseline 0.50, akardite 0.50 & MgO 0.25% (Ref 3, p 89); d) pdr for naval guns: NC (12.2% N) 69.38, DEGDN 25.27, centralite 5.00, graphite 0.10 & MgO 0.25% (Ref 3, p 90)

Refs: 1) CondChemDict (1942), 412
2) Davis (1943), 440
3) O.W. Stickland, General Summary of Explosive Plants, US Office of Tech Services, PB 925 (1945)
4) Anon, "Magnesium Oxide, Calcined (For Use in Ammunition)", MIL-M-14779 (April 1977)

Magnesium Peroxide. See under Peroxides

Magnesium Picrate. See under Picrates

Magnesium Stearate. See under Stearates

Magnesium Stypnate or Magnesium Trinitroresorcinolate. See under Stypnic Acid and Stypnates

Magnesium Sulfate (Epsom Salt, Epsomite), MgSO₄·7H₂O, mw 246.49, color rhomb or monocll cryst, d 1.68g/cc; loses H₂O at 150°, 7H₂O at 200°; v sol in w (72.4g/100g at 0°, 178g at 100°), sl sol in 95% alc & in glycerin. Can be prepd by action of sulfuric acid on Mg oxide, hydroxide or carbonate. Has been used in expls as a temp reducing agent, for example, in Dynamite Grisourette (Reps 1, 2 & 3) contg NG 42–44, Mg sulfate 46–44 and woodmeal 12%

Refs: 1) Marshall 1 (1917), 397
2) Barnett (1919), 140
3) Naoum (1927), 399
4) Melior 4 (1929), 321
5) Davis (1943), 353
6) CondChemDict (1971), 537

Magnesium Trinitroresolate. See under Cresylates

Magnesium Trinitroresorcinolate. See under Stypnic Acid and Stypnates

Magneto Fuse (pronounced Fuze). A medium power electric detonator, invented in 1854 by Abel, which was fired electrically. The original fuze contd a priming mixt of Cu₂O, Cu₂S and K chloride packed around the exposed wire leads, and a main charge of either mealed pdr or MF. It was used primarily in submarine mines. Because of the sensitivity of the fuse, the main charge was replaced with a mixt of powd graphite and MF. At about the same time, an Austrian, Gen von Ebner, independently invented a fuze resembling Abel's, but contg a priming mixt of Sb sulfide 44, K chloride 44 and graphite 12%. Both of these fuzes replaced, in Europe, the Stathom fuse, which had been in use since 1840

Ref: Van Gelder & Schlatter (1927), 741–2

Magneto Exploder (Blasting Machine, Plunge Battery). A small portable electric generator which produces direct current and is manually
operated with a rack and pinion device. It gives a momentary current of high voltage and is used to remotely detonate blasting and demolition charges.

*Ref*: Colver (1918), 547

**Magnus Force (Magnus Effect)**. A sideways thrust acting on a spinning projectile in flight due to the component of the air current acting perpendicular to the axis of the yawing projectile.


**Mahieu Chronograph**. One of the older chronographs, a modification of the Le Boulangès, Bashford and Schultz-Marcel-Dieprez devices.

*Ref*: Barnett (1919), 205

**Maintenance**. In connection with exps and ammunition, maintenance means keeping or maintaining stocks on hand in serviceable condition and ready for immediate issue and use, or to restore them to serviceability if required. Thus, the term maintenance includes inspection, testing, servicing, classifying as to serviceability, repair, rebuilding and reclamation


**Maize Starch** (Indian Corn Starch), \( (\text{C}_6\text{H}_{10}\text{O}_5)_n \), \( \text{mw} \) (162.14)\( _n \), white amorphous powder, does not melt, decomposes when heated in cold \( \text{w} \), \( \text{alc} \) or \( \text{ether} \), forms a jelly with hot \( \text{w} \). Can be prepared from Indian corn by grinding with \( \text{w} \) and stirring the resulting milky liq. On standing, starch settles out and can be separated by decantation. Has been used as a binder in blasting exps to form \( \text{NH}_4 \text{N} \) nitrate agglomerates which when sieved had a bulk d of 0.65g/cc or less.

*Refs*: 1) Hackath’s (1944), 508 2) J. Taylor & V.H. Williams, USP 2218563 (1941) & CA 35, 1229 (1941)

**Maizite**. Excp with a yellow color, resembling that of maize, proposed in 1886 for shell loading. Examples are: a) \( \text{NH}_4 \text{p} \)icrate 60.59, \( \text{NH}_4 \text{n} \)itrate 39.41%; b) \( \text{NH}_4 \text{p} \)icrate 27.76, \( \text{NH}_4 \text{n} \)itrate 72.24%. The latter mix was very insensitive to shock or flame. (Ref 2)

*Refs*: 1) Daniel (1902), 417 2) A. Pérez-Ara (1945), 224 (under Maizitas)

**MALTOSE AND DERIVATIVES**

**Maltose** (malt Sugar), \( \text{C}_{12}\text{H}_{22}\text{O}_{11}\text{H}_2\text{O} \), mw 360.31 when crystd from \( \text{w} \), \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \), mw 342.29 when crystd from alc; the monohydrate exists as colorless needles, dec at about 102\( ^\circ \), d 1.540g/cc; \( \text{v} \) sol in \( \text{w} \), \( \text{sl} \) sol in methanol, less sol in et alc, insol in eth. Prepd by action of diastase (usually malt extract) on starch paste, or by heating equimol mixts of \( \alpha \) and \( \beta \)-glucose in vac at 160\( ^\circ \) (Ref 1)


**Maltose Octanitrate** (Nitromaltose), \( \text{C}_{12}\text{H}_{14}\text{O}_9\text{ONO}_2\text{H}_8 \), mw 702.30, N 15.96%, OB to \( \text{CO}_2 \) – 9.1%, white amorph mass, mp 135\( ^\circ \), dec at 163–64\( ^\circ \) when heated quickly, explds at 171–80\( ^\circ \); d 1.62g/cc (cast); insol in \( \text{w} \), sol in methanol, acet, AcOH and 1:2 eth-alc; \( \text{sl} \) sol in alc. Can be prepd (Ref 5) by mixing 20g of pure maltose (previously dehydrated by heating) with 0.5g of urea nitrate. 60g of 99% nitric acid are added dropwise with stirring and cooling at 0–2\( ^\circ \). To the resulting brown liq, 100g of 25% oleum are gradually added with stirring. This addition should be stopped and the nitrat cooled if any brown fumes start to evolve. After all the oleum is added, the nitrat is warmed to 80\( ^\circ \) and the mixt poured into a large vol of ice \( \text{w} \). The yellow solid ppt is sep’d by filtration and washed sequentially with 1% soda soln and \( \text{w} \). To remove any remaining \( \text{urea} \) nitrate, the ppt is recrystd twice from 1:2 eth-alc and dried. The yield is 159% (31.8g)

Nitromaltose is a powerful exp, being comparable to Tetryl in brisance and Mannitol Hexanitrate in sensitivity to impact. It has been used as a blasting cap charge. (Ref 6). Its thermal stability at 50\( ^\circ \) is comparable to Nitrolactose, with a weight loss of 1.3% after 11 days and
Manganese, Powdered (For Use in Ammunition’), JAN-M-476A (Aug 1948) which specifies the following three grades:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mn</td>
<td>99.5</td>
<td>98.0</td>
<td>95.0</td>
</tr>
<tr>
<td>Free metallic Mn</td>
<td>99.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Granulation:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thru No 200 Sieve</td>
<td></td>
<td>98.0</td>
<td>99.0</td>
</tr>
<tr>
<td>Thru No 230 Sieve</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thru No 325 Sieve</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particles smaller than 10μm diam</td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Grade I is used for delay powders while Grades II and III are for use in pyrotechnic compns. Ref: Mellor 12, 139–200 (1940)

Manganese Azide. See under Azides.

Manganese Dioxide. See Manganese Dioxide.

Manganese Delay Compositions. See Vol 3, D50–D52 under Delay Charges. The D-16 series of delay compns, contg Ba chromate–Pb chromate–Mn, exhibit burning rates in the range of 3–13 sec/inch. As long as mixts of these ingred. do not come in contact with moisture, their storage stability is good. The sensitivity of finely powd Mn to oxidn in the presence of moisture is the underlying cause of erratic stab. Coating Mn with K dichromate or stearic acid, or utilizing treatments such as H₂ reduction or chromic acid are not always satisfactory (Ref 1, 274–5)

Demand for a delay powd capable of withstanding the effects of repeated impacts on a hard surface, typical of skp bombng, lead to the development of Ba chromate–Mn–S compositions. They proved satisfactory in the M16–A1 delay element, with burning times of 8–11 secs obtained with compns contg Ba chromate 70–74, Mn 20–22 and S 3–4%. Storage at 65° resulted in increased burning time,

Maltobenzit. White amor mass, setting point 95°, defgr at about 200°. Prepd by thoroughly blending 10g of Maltose Octanitrate with 5g of m-DNB at 70° in a kneading machine with 20g of benz. The resulting plastic mass is heated to 95° while the kneading is continued, and then cooled. Maltobenzit has the following props: Qe, 936cal/g; Trauzl block test, 260cc; impact sensitivity with 2kg wt, 60–70cm

Mammoth Powder. Gunpowder intended for use in larger cal guns, invented in 1861 by Gen T.J. Rodman. It consisted of conventional BlkPdr, compressed to high density in the form of large grains, in order to render them impermeable to gases under press. These powds were much slower burning than the types previously used (see Black Powder in Vol 2).

Manganese Mn, at wt 54.94, brittle, silvery metal, mp 1245°, bp 2097°, d 7.44g/cc, Mohs hardness 5; decomps in w, readily dissolved in dil mineral acids. Usually associated with Fe ores in sub-marginal concns. Important ores of Mn are pyrolusite, manganite, psilomelane & rhodochrosite. Prepd by reduction of the oxide with Al or C. Pure Mn is obtained electrolytically from sulfate or chloride soln. It is used, in powd form, in the manuf of delay powds and in some pyrotechnic mixts. The requirements of the USA Armed Forces are covered by

although chem analysis showed no appreciable compn change (Ref 1, 268–70)

A review article by Whiting (Ref 2) on the storage stability of Mn delay compns contains 8 refs


**Manganese Dioxide** (Manganese Bioxide, Manganeau Black, Battery Manganese, Manganese Peroxide), MnO₂, mw 86.93, black or dark brown rhombic cryst or amor powd; mp, decomp to Mn₂O₃ & O₂ at 535°, d 5.026g/cc; insol in w, alc and HNO₃, sol in HCl. Found in nature as mineral pyrolusite and as a special African ore of different atomic structure used exclusively for the battery grade. Prep’d by electrolysis, by heating Mn dioxide in the presence of O₂ and by decom’n of Mn nitrate. Used as depolariz in dry cell batteries and in pyrotechnic compns (Ref 2). Is a strong oxid agent and has been used as such in the expl Prométhée, authorized in France as Explosif O no 3 (Ref 1). In the USA a Mil Spec covering Manganese Dioxide (For Use In Pyrotechnics), MIL-M-3281(25 Aug 1950), details min Mn content (55.0%), available oxygen (15.6%), moisture (2.5%) and granulation requirements


**Manganese Nitrate** (Manganous Nitrate), Mn(NO₃)₂·6H₂O, mw 287.04, rose-red monoclinc cryts, mp 26°, bp 129°, d 1.82g/cc; v sol in w, deliq, sol in alc. Can be prep’d by dissolving Mn carbonate in nitric acid. Combines the props of an oxidizer and a flame reducing agent, but has the disadvantage of low mp

Refs: 1) Mellor 12 (1940), 441 2) CondChemDict (1971), 542

**Manganese Oxide.** See under Manganese Dioxide

**Manganese Peroxide.** See under Peroxides

**Manganese Picrate.** See under Picrates

**Manganese Piroxide.** See under Azides

**Manlianite.** A mixt of NH₄ perchlorate 72%, sulfur 13.25 & charcoal 14.75%

Refs: 1) CondChemDict (1942), 290 2) A. Pérez Ara (1945), 219

**Mannans** (Tagut Nut, Corajo, Vegetable Ivory, Carobean), (C₆H₁₀O₅)₃, mw 162.14. Polymeric polysaccharides which yield mannose on hydrolysis. They can be acetylated and nitrated


**Trinitromannan.** Mannan in pure form was obtained from the ivory nut and nitrated, giving nitromannan A & B which gave trinitromannan suitable for artillery use. The products contained both sol & insol fractions

Ref: M.M. Kostевич, Separate, Buenos Aires, Argentina, 14pp (1951) & CA 46 (1952), 9845
MANNITANE AND DERIVATIVE

Mannitane (Anhydride of Mannitol),
\( \text{C}_6\text{H}_12\text{O}(\text{OH})_4 \), mw 164.16; white amorph or cryst powd, mp about 137°; v sol in w, insol in alc.
Can be prepd by heating 1p mannitol with 1.5ps w at 295° in an autoclave for 1.5 hrs. It can be nitrated
Refs: 1) Beil 1, 538, (284) & [611] 2) Daniel (1902), 561

Mannitane Tetranitrate, C\(_6\)H\(_8\)O(ONO\(_2\))\(_4\), mw 344.16, N 16.28%, OB to CO\(_2\) -13.9%; yellowish-brown syrupy liq; insol in w, sol in alc & eth. Can be prepd by gradual dissolution of 1p of manntane in a cooled mixt of 5ps concd nitric acid and 10ps concd sulfuric acid. The slurry is then poured into a large quant of ice w, and the prod sep by filtn, washed & dried. It is a powerful expl with the same impact sensitivity as NG
Refs: 1) Beil 1, 540 2) Daniel (1902), 561 3) Gody (1907), 394

MANNITOL AND DERIVATIVES

Mannitol (d-Mannitol, Mannite, Manna Sugar),
\( \text{CH}_2\text{OH}((\text{CHOH})_4\text{CH}_2\text{OH} \), mw 182.17, colorl rhombic crys, mp 166–68°, bp 290–95° at 3.5mm, d 1.52g/cc, sol in w (13g/100g at 14°), sl sol in alc (0.01g/100g at 14°), insol in eth. Widely distributed in nature, particularly in fungi. Obtained from manna by boiling in alc or by electrolytic redn of glucose. On nitr many yields the expr hexanitrate together with a small amt of pentanitrate (see below)

MANNITOL HEXANITRATE (Nitromannite, or Hexanimannite).

\( \text{CH}_2\text{ONO}_2 \)

\( \text{O}_2\text{NO}–\text{C}–\text{H} \)

\( \text{O}_2\text{NO}–\text{C}–\text{H} \)

\( \text{H}–\text{C}–\text{ONO}_2 \)

\( \text{H}–\text{C}–\text{ONO}_2 \)

Nitromannite (Fr), Nitromannite (Ger & Ital), Mannituzotnikislyy (Russ); \( \text{C}_6\text{H}_8\text{N}_5\text{O}_{18} \); mw 452.17; N 18.59%; OB to CO\(_2\) +7.1% to CO +28.3%; fluffy felted needles from et alc, stout grains by pouring a soln in a w-sol organic solv rapidly into w (Ref 33, pp 236–37); mp 112–13° (Refs 28, 34 & 53), after repeated recrystns from different solvs, mp 109° (Ref 44); cryst d 1.23–1.604g/cc (Refs 2 & 22); CA Registry No 130-39-2 (optical isomer unspecified), 15825-70-4 (prepd from D-mannitol)

Historical. The action of nitric acid on mannitol was first examined by A. Sobrero who isolated the hexanitrate in 1847 (Ref 3). The prepn on a lab scale was repeated by other workers in the mid-19th century (Refs 2, 4, 10 & 12). It was mfd on a small scale in the Royal Arsenal at Turin, Italy until 1853, when 400g expld with great damage (Ref 33, p 198); later work has been described in Refs 13 & 15

Preparation. Nitric acid (d 1.51) in a 300ml Erlenmeyer flsk is cooled with ice-salt to 0°, 10g of mannitol is added in small pieces with swirling at a rate so as to keep the temp at 0°. After all the mannitol is dissolved, 100g of sulfuric acid (d 1.84) is added from a dropping funnel at a rate so that the temp is held below 0°. The porridge-like mass is filtered on a sintered-glass funnel, washed with w, dil Na bicarbonate, and again with w. The crude prod is dissolved in warm et alc, filtered, and cooled to deposit crys of pure Nitromannitol. A second crop is obtained by heating the filtrate and washings to boiling, adding w to turbidity, and cooling; total yield ca 23g (92.4%)(Ref 3, p 236). The nitration of mannitol with nitric acid in trifluoroacetic anhyd has been described in Ref 52, yield 45%. A study of the effect of reaction time, temp, and acid compn on the yield of Nitromannitol is described in Ref 57. The highest yield (96.6%) was obtd with a mixt of 40% nitric acid, 55% sulfuric acid, and 5% w for 1.2 min at 1.67°

The value of the optical rotation was found to decrease with increasing wavelength of light: in ethylene dibromide, wavelength 4359Å, rotation +95.2°; 6716Å, rotation +36.8°. Similarly, in et alc at the same wavelengths the rotations were +87.2° and 32.7° (Ref 22)

Chemical Reactions. Mannitol is regenerated by treatment of the hexanitrate with Amm sulfide (Ref 6), iron in acet ac (Ref 7), ferric chloride (Ref 14), or with hydrogen iodide
(Ref 17). It reduces Fehling's soln (Ref 14 & 15); is decmpd with iron turnings in basic soln with loss of nitro groups (Ref 5); is hydrolyzed with K hydroxide in et alc to give K nitrite (Ref 15). The action of ammonia in eth gives a mixt of a pentanitrate, a tetrani-
trate, and a mannitan tetramerine, C₆H₅O(NH₂)₄ (Ref 8); action of pyridine in boiling et alc forms a pentanitrate (Ref 15). The rate of hydrolysis in 5% K hydroxide or 1% Na carbonate is less than that of Inositol Hexa-
nitrate, NG, or Erythritol Tetranitrate (Ref 38). Treatment with zinc dust and Ac anhydr in pyridine or HCl soln gives mannitol hexacetate (Ref 39); in a similar reaction the same hexa-
acetate is formed when the nitrate is allowed to stand in the cold with Ac anhydr: 100% sulfuric acid 10:1 (Ref 49). The action of pyridine on the hexanitrate gives a pentanitrate whose free hydroxynit group was shown by methy-
lation with Me iodide to be at the 3-position (Refs 50 & 55). Similar results were obtd with an aq acet soln of Aamm carbonate (Ref 54). When mixed with N,N,N',N'-tetramethy-
l-p-phenylenediamine in an organic solv, a violet color develops which indicates that a charge-transfer complex is formed; however, all attempts to iso-
late this complex failed (Ref 64). Similarly in Ref 1, 2404 is a tabulation of complexes formed with a number of org compds including aromatic nitro compds and nitrate esters.

Charge-transfer complexes with pyrimidine and purine bases as well as with solvents like hexa-
methylphosphoramide and dimethyl sulfoxide are reported in Ref 66. The action of aromatic amines (primary, secondary, or tertiary) re-
sulted in fume-offs or unidentifiable tars, in all cases purple or red colors developed prior to more violent reactions (Ref 66)

Analytical. Mannitol Hexanitrate can be hydrolyzed in basic soln and the soln acidified in the presence of NITRON to quantity ppt NITRON nitrate (Ref 16). A procedure is de-
scribed for the quant detn of nitrate esters, including Mannitol Hexanitrate, in the presence of aromatic nitro compds in Ref 17. It gives a yellow color when treated in et alc or acet with 5% aq K hydroxide, then 5% aq ammonia (Ref 24). It can be quantity detd by reduction with Devarda's alloy (Encycl 8, D-1110) or Al wire in aq et alc and titration of the evolved

ammonia (Ref 25). In a similar procedure the ester is hydrolytically reduced and the mannitol quan-
ity oxidized with periodate (Ref 37). It is detd by reaction with 4-hydroxy-m-xylene in 72% sulfuric acid followed by spectrophoto-
metric analysis of the 5-nitro-4-hydroxy-m-xylene formed (Ref 43). A rapid thin-layer chromatog sep and quant detn of mixts of Mannitol Hexanitrate with other exps is de-
scribed in Ref 62. The polargraphic analysis of Mannitol Hexanitrate is described in Refs 59 & 67, the compd was found to give a peak potential at ~0.35 v, limit of deton 5μg/ml Briscane – Sand Test. 121.5–143% of TNT (Refs 18 & 30); 225% of MF (Ref 23) (See also Encycl 2, B280 & B298)

Lead Plate Cutting Test. 116–19% of TNT (Ref 30) (See also Encycl 2, B280)

Detonation Rate. 7000m/sec at d of 1.5g/cc in an iron pipe 25mm in diameter and a wall thickness of 5mm (Ref 20, p 249) (See also Encycl 2, B280)

Explosion Temperature. It expl spontaneously at 160–70⁰ (Ref 18); in 1 sec at 232⁰ (Ref 19); in 5 secs at 175⁰ (Ref 26); deflagration temp 185⁰ (Ref 51)

Flammability Order. It is not ignited by the spit of a BkPdr fuse, contact with a lighted match causes deton (Ref 20, p 249)

Fricion Pendulum Test. Unaffected by fiber shoe, steel shoe causes deton (Ref 18); 3cm for 50% expl with 4kg wt (PETN 12cm) (details of test in Ref 35, pp 12 & 13)

Gas Evolved on Heating. At 100⁰ after 1 hour gas evolution was 2.62, after 2 hours 3.69, and after 5 hours 6.75 L/kg (Ref 45)

Heat of Combustion. –674.9kcal/mole (Ref 32); –1521cal/g (Ref 45); –1484.2 ± 5.8cal/g (purity by nitrometer 99.46%) (Ref 47, p 22); –1565 cal/g (Ref 46); –1525cal/g, Qᵥ –689.5kcal/ mole, Qₒ –683.7kcal/mole (Ref 31); – 1515 cal/g (Ref 29)

Heat of Explosion. Caled –1459, found –1454 cal/g (Ref 60)

Heat of Formation. –165.2kcal/mole (Ref 32); –169.42 ± 0.88kcal/mole (Ref 47)

Heat Test at 100⁰. Frothed in 48 hours, expld in 100 (Ref 46)

Hygroscopicity. 0.17% wt gain at 30⁰ and 90% RH (Ref 46)

Ignition Temperature. 165⁰ (Ref 45)
Impact Sensitivity. BM app 8–11 cm (Refs 42, 45 & 46); PA app 4 inches (11 mg sample) (Ref 46)

International Heat Test at 75°. 0.4% wt loss in 48 hours (Ref 46)

KI Test. 6 min for color at 65.5° (Ref 46)

Power by Trauzl Test. 102% of NG (Ref 20, p 156); 172% of TNT (Ref 26); 150% of PA (Ref 34); 131% of Tetryl (Ref 30)

Sensitivity to Ignition by Shock Wave. When initiated with Melinite (70% PA, 30% NC), it was found to have a shock wave sensy similar to PETN (Ref 51)

Sliding Rod Impact Test. In Ref 36 is a table of heights of fall for 50% explos listed against sample size and angle of fall; extreme values are 0.2 cm for 3 mg sample at 75°, and 25.5 cm for 62 mg at 30° angle

Specific Volume of Gases Formed on Explosion. 723 ml/g (NG 712 ml) (Ref 46)

Stabilization. Chromatographically pure Mannit Hexanitrate was mixed with varying percentages of 22 stabilizers and the mixtures tested for stability in the 100° heat test; best results were obtained with a mix of 96% MHN, 2% Anm oxalate, and 2% dicyandiamide (4.07% wt loss after 48 hours, 5.74% after 96 hours) (Ref 56). The use of ethylene oxide as a stabilizer is reported in Ref 27

Thermal Decomposition. Slow heating causes decomn at 150° with evolution of red fumes (Ref 20, p 249)

Vacuum Stability. When heated to 100° for 1 hour, 2.62; 2 hours, 3.69; and 5 hours, 6.75 ml/g of gas are evolved (Ref 45)

Solubility. Insol in w (Ref 8); sol in warm et alc, eth, and acet ac (Ref 11). It is very sol in acet, hot et alc, and hot me alc (Ref 44); solys are: 0.012g/100 ml in w at 25°, 2.356g/100 ml of et alc at 25°, and 3.394g/100 ml of acet at 25° (Ref 45). Solns in acet exhibit a large negative deviation of the vapor pressure from ideality. It is presumably caused by H-bonding betw the acet molecules and the H-atoms on carbon bearing nitroxy group (Ref 40)

Stability in Storage. It can be stabilized in storage by the addn of 5–10% Na, K, or Li salicylates (Ref 63)

Uses: It can be used as a secondary charge in detonators replacing Tetryl. Mixts with Diazonitrophenol (Encycl 2, B59) or Tetrazene are detonators (Ref 41). Use is claimed as a safety blastcap, as it will only transmit combstn after being confined by crimping a fuse on the cap (Ref 41). It is claimed to be an oxidizer in a solid propnt formulation (Ref 38). An 80/20 mixt with Tetrazene coated with 2% PVA can be hot molded to form propelling charges or primers (Ref 65). It has been incorporated at a level of 10% in an expnl rocket grain formulation whose strand burning rate was 0.3 inches/sec at 1000 psi (Ref 48). There is an extensive literature on the drug use of Hexanitromannit which action is similar to NG (See article in Ref 61 and references therein)

Written by C.H. McDonnell

M 16


Mannitol Pentanitrate (Pentanitromannit), CsH8(OH)(ONO2)3, mw 407.16, N 17.20%, OB to CO2 -1.96%, color needles from alc, mp 77-79°; v sl sol in w (0.00033g/100g at 15°, 0.002g at 60°), sl sol in alc (1.67g/100g at 12.8°) and eth (1.31g/100g at 9°). First prepd in 1864 (Ref 1), together with mannitol tetranitrate, by passing NH3 gas thru an eth soln of mannitol hexanitrate. It was later obtained (Ref 2) from the mother liquor remaining after crystn of crude mannitol hexanitrate (obtd by nitration of mannitol with mixed nitric-sulfuric acid) from alc. About 2.5g of mannitol pentanitrate were obtd from 25g of crude hexanitrate. Defgr mildly on heating, more strongly on impact

Refs: 1) Beil 1, 542 2) J.H. Wigner, Ber 36, 796 (1903) 3) L.D. Hayward, JACS 73, 1974-75 (1951)

**D-MANNOSE AND DERIVATIVE**

_D-Mannose_ (Seminose), CH2OH(CHOH)4CHO, mw 180.16, mp 132° (dec), d 1.53g/cc; v sol in w (248g/100g at 17°), v sl sol in abs alc, insol in eth. A carbohydrate occurring in some plant polysaccharides. Can be prepd by hydrolysis of mannanes by dil acids or by certain enzymes or microorganisms. It is an isomer of glucose. On nitration, it yields an expl compd (see below)

*Ref*: Beil 1, 905, (456) & [902]
D-Mannose Pentanitrate (Nitromannose), C<sub>6</sub>H<sub>7</sub>O(ONO<sub>2</sub>)<sub>5</sub>, mw 405.16, N 17.29%, mp 81–82°, bp dec at about 124°, insol in w, sol in alc, and reduces Fehling's soln slowly on warming. Can be prepd by dissolving d-mannose in cold concd nitric acid and then adding concd sulfuric acid. It is an expl which is unstable at even slightly elevated temps, decomps rapidly when stored at 50°, losing 46% by weight in 24 hours
Refs: 1) Beil 1, 907 2) W. Will & F. Lenze, Ber 31, 76 (1898) 3) Davis (1943), 241


Manonitrometer. An apparatus for detg N content of NC, mixed acids, etc
Ref: M.F. Planchon, SS 11, 22–24 (1916)

Manuelles. Expls patented in France in 1891 by Magnier, de Lom de Berg and Vieillard. Consisted of mixts of Amm or Na picrate with Amm or K nitrate in various proportions. They could be blended with resinous hydrocarbons for plastic consistency
Ref: Daniel (1902), 416–17

Maquenne Block. See under Melting Point Determinations

Marble. A variety of limestone (CaCO<sub>3</sub>). It is a hard, very s porous stone, which occurs in nature in many forms and colors. It may be prepd artificially by the recryst of limestone under great press and at high temp. In powd form it has been used as an antacid ingredient of some Dynamites (see under). Silberbard (Refs 1 & 2) proposed its use for purification of nitrated hydrocarbons by refluxing the material to be purified with marble or dolomite

Marin's Explosives. Expls contg typically Amm perchlorate 32.2–34, Gu nitrate 24–26, Na nitrate 24.6–25, TNT 4–5.6 and liq di- or trinitrotoluenes 11–13.6%
Refs: 1) Daniel (1902), 418 2) BritP 121294 (1918) & CA 13, 753 (1919)

Marine Fiber (Posidonia). Fibrous material obtained from the marine plant Posidonia Australis, found in Spencer's Gulf, south Australia. It consists of short, harsh fibers, resembling jute in appearance, and contains about 56% cellulose and 16% ash. When the crude fiber is purified by boiling with caustics and acids, the resulting prod contains less than 1% ash and is suitable for the prep of an expl nitrate (see below). The idea of utilizing marine fiber for this purpose was raised during WWI since the cultivation of cotton was not successful in Australia because of the high cost and shortage of labor

Nitrate Marine Fiber (Nitroposidonia). Prepd by gradually adding the previously purified and dried fiber to sufficient mixed acid, consisting of 1 part by wt nitric acid (d 1.59/g/cc) and 3 parts sulfuric acid (d 1.84/g/cc). After 72 hrs of nitration, the prod was sepd by filter, washed and boiled with w for a much shorter time period than required for the stabilization of cotton NC. The yield of purified prod was 72% and contd 12.3% N. Stability by Abel's test at 76.6° was 10.5 mins compared with 15 mins for regular guncotton. When mixed with regular ingredients of smokeless powd, it gave a prod resembling in all its properties smokeless powds produced with cotton NC
Refs: 1) B.J. Smart, ChemEngMinReview (Australia) 10, 380 (1918) & CA 13, 262 (1919) 2) B.J. Smart & P. Pecover, JSCI 37, 300–01 (1918)
Marking of Ammunition and Containers for Ammunition and Explosives. Ammo is identified completely by painting and marking, which includes the ammo lot number, on original packing containers. Once removed from its packing, ammo may be identified by painting and marking on ammo items. To identify a particular design, a model designation is assigned at the time the model is classified as an adopted type. This model designation becomes an essential part of the nomenclature and is included in the marking of the item. Prior to WWI, the year in which the design was adopted (preceded by an M) was used as the model designation; for example, M1914. From WWI to 1 July 1925, it was the practice to assign mark numbers; that is, the word “mark”, abbreviated “Mk”, followed by a Roman numeral. The modification was indicated by the addition of M1 to the mark number, the second by MII, etc. However, the use of Roman numerals has been discontinued and all future reference and records will be in Arabic numerals. The present system of model designation consists of the letter “M” followed by an Arabic numeral, for example, “M1”. Modifications are indicated by adding the letter “A” and the appropriate Arabic numeral. Thus, “M1A1” indicates the first modification of an item for which the original model designation was “M1”. Wherever a “B” suffix appears in a model designation, it indicates an item of alternative or substitute design, material or manufacture.

When ammo is manufactured, an ammunition lot number is assigned in accordance with pertinent specifications. As an essential part of the marking, this lot number is stamped or marked on the item, size permitting, as well as on all packing containers. It is required for all purposes of record, including reports on condition, functioning, and accidents, in which the ammo is involved. To provide for the most uniform functioning, all of the components in any one lot are manufactured under as nearly identical conditions as practicable.

Ammo is packed and packing containers are marked in accordance with applicable drawings and specifications. Containers are designed to withstand conditions normally encountered in handling, storage and transportation, and to comply with ICC regulation. Marking of containers includes all information required for complete identification of their contents and for compliance with ICC regulations.


Marksman Powder. An American variety of EC rifle powd, developed about 1900, for midrange shooting in .22 Cal rifles
Ref: Van Gelder & Schlatter (1927), 800

Marqueyrrol’s Stability Test. 200g samples of double-base powds were heated at 50° under vac in a round bottom Pyrex flask. Every 3–4 days, the vapors were pumped out, collected in a gasometer over Hg and measured. The test was contd until the powd started to decom very rapidly, usually after 1800–2000 days. A curve was then plotted of cc of gas evolved vs days of heating, and the gas was analyzed for CO₂ and NO. If any liq formed, it was collected, measured and analyzed.

A stable powd, such as one contg NC (11.97% N) 71.98, NG 22.20, vaseline 4.87 and DPhA 0.97%, evolved 35.5cc of gas and 4.75ml liq after 1834 days with a wt loss of 2.55g. The gas contd CO₂ 39.7, NO 19.0%, plus other ingridients, and the liq consisted mostly of acet.

Some French powds which were stabilized with amyl phthalate, eg, NC (11.89% N) 72.1, NG 22.8 and amyl phthalate 5.1%, evolved 298cc of gas plus 6.9ml liq after 1834 days with a wt loss of 3.55g. Compn of the gas was CO₂ 31.3, NO 30.0%, plus other ingridients, and the liq consisted mostly of acet.

Refs: 1) M. Marqueyrrol, MP 23, 178–182 (1928) 2) Reilly (1938), 90

Mass, Specific, of Constituents of Smokeless Propellant. Literature data on the specific mass of over 100 compds are given in Ref. Kopps additive rule applies with an error generally less than 1%, eg, 1/d = Σ (ni/pi), where ni is % of constituent, pi is specific mass of constituent, and d is specific mass of propellant.
MASS SPECTROMETRY

Definition and Terminology: A mass Spectrometer is an instrument which produces a beam of ions from a given sample and separates the ions according to their mass-to-charge \((m/e)\) ratios. A record of the relative abundance of the ionic species arranged according to their masses constitutes a mass spectrum. Historically, the instrumentation to achieve this has developed along two principal lines, one concerned chiefly with the measurement of relative abundances of ionic species and the other with the determination of their accurate masses. These two kinds of instruments became known as mass spectrometers and mass spectrographs, respectively. Until recently, the mass spectrographs, as the name implies, used a photographic recording technique to register the ion beam, while mass spectrometers relied on measurement of ion current and electronic amplification. However, modern instruments with dual electrical-photographic detection make the distinction less meaningful and current practice is to use the generic terms such as “mass spectrometer” and “mass spectrometry”.

Every mass spectrometer consists of four principal components (Fig 1): (1) the source, where a beam of gaseous ions are produced from the sample; (2) the analyzer, where the ion beam is resolved into its characteristic mass species; (3) the detector, where the ions are detected and their intensities measured; (4) the sample introduction system to vaporize and admit the sample into the ion source. There is a wide variety in each of these components and only those types which are relevant to analytical and organic mass spectrometry will be emphasized in this survey. The instrumentation aspects will be discussed after the ionization process and the basic ideas of mass spectrometry are considered first (Refs 7 & 30).

The Ionization Process: Electron “bombardment” or “impact” of the gaseous sample at low pressures (10⁻⁶ to 10⁻⁸ torr) is the most common means to generate ions. While it is possible to study both positive and negative ions in mass spectrometry, most of the investigations are designed to study the positive ions since these are produced in much larger numbers than the negative ions under electronic impact. For a sample atom or molecule to be ionized a certain minimum energy characterized by its “ionization potential” has to be supplied. The minimum amount to remove the least strongly bound electron from a gaseous atom or molecule is called the ionization potential. The loss of a single electron by most atoms and organic molecules takes energy in the range 5 to 15 ev and the ions so obtained are referred to as “molecular ions” or “parent ions” in mass spectrometric usage. Occasionally, doubly charged ions are formed in the ionization which exhibit an apparent “mass” one-half of the corresponding singly charged ion because the mass analyzer is responsive only to mass-to-charge \((m/e)\) ratio. However, the vast majority of the ions are singly charged, justifying the imprecise use of the term “mass” in place of \(m/e\) in everyday mass spectrometry. With energy available in excess of ionization, the molecular ions dissociate to ions of smaller mass. The minimum energy for the appearance of a given “fragment ion” is called the “appearance potential.” Since most ionization sources use 70 ev electrons, considerable fragmentation of molecular ions takes place resulting in a series of product ions. The mass spectrum \((m/e\) vs relative abundance\) of a
sample can therefore serve as a "fingerprint" of the substance under study and help its characterization in terms of molecular weight, elemental composition and the manner in which atoms are grouped together within its structure. For illustration, the mass spectrum (Ref 30) of carbon dioxide is shown in Figure 2. In this the abscissa is an m/e scale (atomic mass units, amu) and the ordinate shows relative ion abundances. For example, the relative abundance of the ion, m/e = 28 is four times that of the ion, m/e = 22 from a comparison of the peak heights and the corresponding scale factors.

**Uses of the Mass Spectrum:** There are three uses in general for mass spectral information: (a) **Determination of masses of ions:** An example is the carbon dioxide spectrum (Fig 2) where it is adequate to obtain masses in nearest integral numbers. In other cases, the precise mass of ions with an accuracy of a few parts per million may be required to investigate molecular weight, elemental composition and structural details. (b) **Determination of isotopic abundance:** This information can be applied in such diverse areas as isotopic constitution of elements, geochronometry, isotopic dilution analysis and the study of reaction mechanisms by isotopic tracers. (c) **Mass spectral patterns:** The array of peaks in the complete spectrum of a pure substance is referred to as a cracking pattern. Fig 3 shows a line diagram (bar graph) of the mass spectral pattern of methane (Ref 29). If this were an unknown substance it would be obvious from the spectrum that this represents a structure with molecular weight 16. Peaks at masses 15, 14, 13 and 12 show successive loss of fragments of mass 1, 2, 3 and 4 from the molecule and must correspond to the loss of four hydrogens. The remaining fragment of mass 12 can only be a carbon atom, and the unknown is identified as methane. For larger molecules the spectra and their identification becomes more complicated. Mass spectral patterns may also be presented as tables of m/e and relative abundance as illustrated by that of dimethylmethane (Table 1, Ref 44). These cracking patterns can be utilized for a variety of purposes in qualitative and quantitative analysis and structural determinations. Cracking patterns for thousands of compounds have been obtained, and there are a number of compilations available (Refs 12, 19 & 32).

![Mass spectrum of carbon dioxide. Relative peak intensities are plotted against m/e.](image)
Historical: That positive rays could be deflected in electric and magnetic fields was shown as early as 1898 by Wien, but it was not until 1912 that what was to become the forerunner of the modern mass spectrometers was built by J.J. Thompson, who became known as the "father" of mass spectrometry. The existence of two isotopes of neon (m/e 20 and 22) was demonstrated by Thompson with this instrument. The discovery of stable isotopes of elements has been generally considered the greatest achievement of mass spectrometry because of its profound effect on our understanding of the structure of the atom and the properties of elements. The next few years saw the construction of more sophisticated instruments by Dempster (1918) and Aston (1919). Aston's instrument, in particular, suited the determination of exact mass of nucleids, and enabled him to measure the whole number divergence of nucleic masses of many elements, that led to the important concept of "packing fractions".

Table 1

<table>
<thead>
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<th>Mass/Charge Ratio</th>
<th>Relative Abundance</th>
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Fig 3. The mass spectrum of methane.
During the next 20 years major advances in the field of electronics made it possible to construct reliable, accurate and easy to handle mass spectrometers. The remarkable reproducibility of light hydrocarbon mass spectra soon led to the acceptance of mass spectrometry as a tool for quantitative analysis (Ref 1); especially of hydrocarbon mixtures, valuable to the petroleum industry. Nier's isotope-ratio analyzer in the early 40's, which paved the way for the separation of uranium isotopes 235 and 238 and the development of nuclear energy, was the next milestone in mass spectrometry. In recent years great strides were made in the sensitivity, resolving power and precision in mass measurement, with the result that application of high resolution techniques to organic structure elucidation has become the most active area in mass spectrometry. The advent of computer based data acquisition and processing has further led to automation techniques for the generation and analysis of massive amounts of data

**Instrumentation:** Several fundamentally different types of ion sources and mass analyzers are currently available and employed in mass spectrometers depending on their application. There appears to be much less of a diversity in detectors and sample handling systems. A detailed account of all the types may be found in a number of monographs (Refs 7, 16, 29, 30 & 64), while Refs 49 & 55 give most recent reviews of ionization sources. Ionization sources which use electron bombardment and analyzers which use magnetic and electrostatic focusing are the common types used in organic analytical mass spectrometry, and these were also the earliest types. This survey will describe only the common types in some detail. However, a brief description of several new ion sources is included for two reasons: first, the mode of ion production generally determines the application of the instrument, and second, a variety of new sources are being applied to expls and proplnts

**Ionization Sources**

(a) *Electron Bombardment*: In the vast majority of organic analytical instruments today, ions are produced by the collision of electrons with sample molecules in the gas phase. This results in a Franck-Condon transition producing a molecular ion, an odd electron ion, usually in a high state of electronic and vibrational excitation. This excitation and its distribution over various modes of decomposition of the molecule determine the resultant fragmentation pattern.

Fig 4 is a diagram of an electron "impact" source. The sample vapor is admitted into the ion source thru the slit in the back of the chamber and it passes thru a collimated electron beam 'b'. On impact of electrons with the neutral molecules, positive ions (to a small extent negative ions) are produced. A small positive potential ("repeller potential") between the back wall 'c' of the ion source and first accelerator plate 'd', expels the positive ions toward the accelerating region and at the same time attracts the negative ions which are then discharged at repeller plate 'c'. The positive ions are accelerated by the potential difference applied to plates 'd' and 'c', pass thru the exit slit 'f' and continue toward the collector.
The energy of the electron beam (the potential difference between filament 'g' and the area of impact) is adjusted to 70 ev for maximum ionization efficiency, but it can be varied by appropriate choice of potential difference between the heated filament 'g' and anode 'h'. In the region 50 to 80 ev the peak heights are insensitive to fluctuations in the ionization voltage by a few volts, and reproducible cracking patterns are thus obtained. Ionization and appearance potentials may be determined by scanning the mass spectrum at increasing ionizing voltages in the 5–20 ev range. At a constant sample pressure the number of ions formed and, therefore, the peak heights, are directly proportional to the electron current passing thru the vapor. By adjusting the ionizing current the intensity of the spectrum can be varied. Electron impact sources are the most reliable and highly developed ionization methods. A high yield of ions, good energy homogeneity and stable ion beam are some of its advantages. Samples as little as 0.1 ml of gas or about 1 microgram of solids can be routinely analyzed. However, a serious limitation of the electron impact source is that a 70 ev electron beam is an extremely drastic method of ionizing a sample. As a result of the extensive fragmentation that follows, often including the loss of the molecular ion, vital information about the structure of the intact molecule is destroyed. Some of the newer ionization methods described below obviate this problem and have therefore become attractive to chemists.

(b) Chemical Ionization: Chemical ionization (CI) is perhaps the most popular among the newer techniques in mass spectrometry (Refs 49 & 55). In contrast to the electron impact (EI) source, a CI source offers the advantage of simple cracking patterns, intense quasi-molecular ions and easy to interpret spectra. In the CI technique a reactant gas such as methane is introduced into the source at a relatively high pressure (1 torr) along with a very much smaller amount of sample. The primary ionization occurs in the normal way by electron impact in the reactant gas. The primary ions then give rise to ion molecule reactions with neutral molecules of the reactant leading to secondary ions. The secondary ions, predominantly $\text{CH}_3^+$, $\text{C}_2\text{H}_5^+$ and $\text{C}_3\text{H}_5^+$ in the case of methane react by proton or hydride ion transfer with the sample molecules and convert them to positively charged ionic species which are then mass analyzed.

**Primary ions:** $\text{CH}_4 + e \rightarrow \text{CH}_4^+ + \text{CH}_3^+; \text{CH}_2^+$ etc

**Secondary ions:** $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_4^+ + \text{CH}_3$

$\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$

**Ionization of Sample, MH:**

$\text{CH}_3^+ + \text{MH} \rightarrow \text{CH}_4 + \text{MH}_2^+ (\text{QM})^+$

$\text{C}_2\text{H}_5^+ + \text{MH} \rightarrow \text{C}_2\text{H}_6 + \text{M}^+$ or

$\rightarrow \text{C}_2\text{H}_4 + \text{M}^+ + \text{H}_2$ etc

A source design of this type is shown in Fig 5.

A significant difference between the CI and EI processes is that the energy available in these ion-molecule collisions tends to be somewhat lower, having a profound effect on the fragmentation patterns which provide much of the structural information about the sample molecule. Compounds which do not normally show a molecular ion in EI mass spectrometry are observed to yield a quasimolecular ion (QM) at one mass unit higher than the molecular weight due to addition of a proton. The CI spectrum is therefore quite useful in situations where rapid identification of compounds within a specific class needs to be made, especially if these compounds do not give molecular ions under EI conditions. Examples of other reagent gases used in CI are hydrogen, isobutane and water vapor.

An important additional feature of CI spectroscopy is its ability to handle gas chromatographic (GC) effluents directly if a proper reagent gas is used as the carrier gas in the GC. (This arrangement is also shown in Fig 5). Under these conditions the GC-CI system is quite simple and does not require an interfacing device to eliminate the carrier gas.

Chemical ionization mass spectrometry has rapidly found extensive application to many substances (Refs 15, 23 & 28). Of particular importance is identification of complex and
dangerous drugs (Refs 36, 40, 41, 46, 51, 60 & 72), as well as forensic identification of expls (Refs 69, 70 & 71). The EI mass spectra of expls contain a large number of fragment ions and almost no molecular ion, thus making the identification difficult. The CI spectra of these expls resolve the identification in several instances due to the observed quasimolecular ions (Refs 69, 70 & 71). The EI and CI (isobutane) spectra of RDX shown in Figs 6 and 6a illustrate the point about molecular ions. Some explosives however, do not yield a quasimolecular ion but the spectra still contain characteristic fragment ions giving supplementary information to EI spectra. In addition, chemical ionization offers a unique advantage to exploit a variety of reactions possible with different reagent gases to establish structure-reactivity relationships.

(c) Atmospheric Pressure Ionization: Atmospheric pressure ionization (API) mass spectrometry (Refs 8 & 66) and ion cluster mass spectrometry (ICMS) to be described later (see below) are akin to chemical ionization (CI) mass spectrometry in that all three rely upon mass analysis of ions which are products of ion-molecule reactions occurring in a reactant
Fig 6
Fig 6a
gas in the ion source. As the name implies, API mass spectrometry depends upon ion-molecule reactions occurring in the reactant gas at atmospheric pressure. The ionization reactions are initiated in a flowing gas stream by electrons from a radioactive $^{63}$Ni source. The sample, dissolved in a suitable organic solvent, is injected directly into the source. Both positive ions, eg, $M^+$ and $MH^+$, and negative ions, eg, $(M-H)^-$, are formed by a series of complex ion-molecule reactions. The ions are made to exit thru an aperture and subjected to mass analysis. The source, being very small in volume (0.025 cm$^3$), is compatible with gas chromatography capillary columns to which it can be interfaced. It is claimed that as little as 150 femtograms of sample can be readily detected. This method has been applied with success to the analysis of drug metabolites and other compounds of biological interest. A substantially similar technique employing a 100 millicurie polonium alpha-particle source for ionization was reported earlier

(d) Ion Cluster Mass Spectrometry (ICM): This relatively new technique (Ref 65) is an outgrowth of studies of ion-dipole clusters in the gas phase and uses hydrated proton species, $^1\text{H}(\text{H}_2\text{O})_n$ to serve as precursors for ion clusters of a sample molecule, $\text{H}^+(\text{H}_2\text{O})_n(A)_m$, where A represents the sample molecule. The hydrated protons are formed via ion-molecule reactions with primary ions such as $^4\text{N}_2$ and $^4\text{O}_2$, which in turn may be generated by several methods including corona discharges. In the presently reported method air or nitrogen containing trace quantities of water vapor and the substance to be analyzed flow into the ion source which is a corona discharge cylinder. The discharge between a coaxial wire (0.08 mm, 90% Pt + 10% Rh) and a 12 mm I.D. stainless steel cylinder is maintained at 10 Torr with a 6 kv power supply. The ions are extracted from the source chamber by diffusion thru a 35 micron orifice and subsequently mass analyzed. The virtues of this technique are stated to be absence of a spectrum complicated with fragment ions, high mass peaks directly related to the molecular weight, and sensitivity well below the ppm concentration range. An obvious area of application appears to be pollutant analysis

(e) Fission Fragment Ionization Source (FFI): Mass spectrometry is powerless to deal with compounds that are inherently nonvolatile such as polypeptides and polysaccharides. In a very novel adaptation of the familiar means of ionization with a radioactive source, McFarlane and Torgerson used fission fragments from Californium-252. The sample was deposited on a micron thick sheet of nickel foil placed close to a Cf-252 source. The fission fragments passing thru the Ni-foil create localized temperature in the range 20,000-30,000$^\circ$K for about 10$^{-11}$ second. The high temperatures vaporize impurities such as $\text{H}^+$, $\text{Na}^+$ and $\text{H}^-$ in both the sample and the nickel. These secondary ions react with heated sample molecules to produce quasimolecular ions. A notable achievement of this technique was to obtain a spectrum showing the quasimolecular ion of vitamin $\text{B}_12$. This unique method has a potential for application to unstable expl materials analysis (Ref 76)

(f) Photoionization: Ionization of molecules may also be accomplished with ultraviolet radiation of sufficiently short wavelength (Refs 30 & 49). Since ionization potentials of most elements and compounds are in the 10-25 ev range, the wavelengths required are 1200 $\AA$ or less. Photoionization sources are similar in principle to electron impact sources in that the neutral gas molecules are "bombarded" with UV light in the ionization chamber at 10$^{-4}$ to 10$^{-6}$ torr. A discharge thru krypton or hydrogen at a few mm pressure provides continuous ultraviolet radiation. The photoionization cross-sections are one or two orders of magnitude less than those for 70 ev electron impact. Electron multiplier detection (see below) is therefore essential. Generally, photoionization yields mass spectra which are similar to those from electron impact at the same energy. Monochromatic UV sources enable very accurate determination of ionization and appearance potentials

(g) Spark Source: The vacuum spark ion source is best suited for elemental impurity analysis of solids at very low levels, (Refs 6b, 30 & 64) with the result that it derived a natural stimulus from the growth in semiconductor and reactor materials technology. The technique is known for its high sensitivity (limit of detection, 0.001 ppb) and a complete coverage of elements, and it is the method of choice today for impurity analysis of solids. There are three variations in
the sparking technique, namely, the radio-frequency (rf) spark, vacuum vibrator and pulsed dc arc. The basic principle in all of them is a potential build-up between the electrodes of the material to be analyzed until discharge takes place. The rf spark is the most common one among the three types, and an instrument with this source has recently been employed to analyze impurities in exphs (Refs 68 & 75). The technique, however, suffers from the disadvantage of requiring complex and expensive instrumentation including a photoplate recording device.

**Field Ionization Source:** Electrical fields of the order of $10^8$ volts/m can be caused to produce positive ions from atoms and molecules (Ref 5). The ionization occurs by a strong interaction between the field and the outer electron shell of neutral molecules. These very large electric fields can be obtained by holding very fine metal points at high potentials. In early instruments (Ref 5), for example, the field was set up near a $5 \times 10^{-5}$ cm radius metal tip with a potential of 10 kv between the anode and the cathode. An aperture in the cathode was used to extract the ions. When the metal tip is positive, the strong electrostatic field results in the removal of ions of impurities adsorbed on the surface of the metal, or ions may be produced from impinging gas molecules. When the field ionization occurs in the gas phase near the emitter, continuous ion current results. Recently Beckey (Ref 9) replaced the metal tip with a platinum wire of 2.5 microns diameter and 5 mm long placed parallel to the cathode diaphragm. An arrangement of this type is shown in Fig 7 which represents both field and electron impact sources within the same source system.

Inghram and Gomer showed that the mass spectra of molecules were much simpler using a field ionization source than with an electron bombardment ion source. Mainly parent ions are formed, unlike under electron impact which gives rise to considerable fragmentation. The simplicity of the mass spectra offers obvious applications in analysis of complex organic mixtures and their use is likely to become widespread.

**Surface Ionization:** Similar to field ionization in principle is surface ionization (Refs 30 & 55) which employs an an ionization element consisting of a hot ribbon of a metal with a high work function (tungsten) coated with the sample. At sufficiently high temp, emission of a neutral vapor accompanied by positive ions takes place. Some of the atoms and molecules of the sample will have lost an electron to the surface particularly if the compound has a low ionization potential. This approach is suitable only to nonvolatile inorganic salts and it tends to be less destructive to the sample than the spark source. Because it is selective only to the coated material, it produces extremely clean spectra.

For the analysis of surfaces there are a group of ion bombardment techniques based on "sputtering" processes described in Ref 30. Since the spectra obtained consists mainly of adsorbed gases and radicals, these techniques are omitted from this discussion.

**Negative Ion Mass Spectrometry:** As mentioned earlier, electron impact ionization yields some negative ions along with the positive ions even though their number is smaller by about a factor of 1000. Because of this low yield their use in chemical analysis has been very limited. The low yield of negative ions arises from the fact that with 70 ev electrons the negative ions are formed by the capture of secondary electrons, and that a number of reactions such as

![Combined electron impact and field emission source](image_url)
electron capture giving negative ions occur below 20 ev. Also, the negative ion spectra exhibit a strong dependence on source pressures.

Despite the above limitations, negative ion analysis offers a possible advantage in electron-negative compound analysis and several attempts have been reported (Refs 37, 47 & 48) recently to use high resolution mass spectrometers for negative ion studies using 70 ev electrons and source pressures below 10^{-6} torr. Since many expls are nitro compounds which are strongly electro-negative compounds, negative ion mass spectrometry seems to be an attractive method. A successful technique has been published by Yvon and Boettger (Ref 56a & 57) who modified an Associated Electrical Industries Model MS9 instrument to perform negative ion analysis over a wide range of electron energies and source pressures. They obtained negative ion spectra of nitrobenzene and TNT. Because of its selectivity and sensitivity, this method is well suited to detect TNT in concealed areas such as airline baggage (Ref 56a).

Mass Analyzers

The heart of the mass spectrometer is the mass analyzer, the function of which is to measure the mass-to-charge ratios of ions and provide a means of their identification. This is achieved by a combination of a dispersive action to separate the ions according to their m/e ratios and a focusing action to maximize the resolved ion intensities.

All analyzers use one or more of three basic principles: (a) magnetic analysis, (b) electrostatic analysis, and (c) time-of-flight analysis. Magnetic analyzers of single and double focusing types are by far the most common ones currently in use, and will serve to illustrate the methods of analysis. Two other types of analyzers which have gained popularity for analytical applications but are omitted in the following discussion, are the time-of-flight mass,

\[ T_{\text{kin}} = \frac{1}{2}mv^2 = eV \]  
(Eq 1)

\[ HeV = \frac{mv^2}{r} \]  
(Eq 2)

\[ m/e = \frac{H^2r^2}{2V} \]  
(Eq 3)

Only those ions following a path which coincide with the arc of the analyzer tube in the magnetic field will be brought to a focus on the detector slit. To obtain a mass spectrum, either the magnetic field or the accelerating voltage is varied continuously so as to bring ions of varying m/e into focus successively. For proper functioning, the ion source and the path thru which the ions travel to the collector have to be kept under very low pressure of the order of 10^{-7} torr.

The effectiveness of mass separation achieved by the analyzer is expressed as resolution \( R \), defined by the equation

\[ R = \frac{M}{\Delta M} \]  
(Eq 4)

where \( M \) is the mass of the first recorder peak in a doublet of equal size peaks, and \( \Delta M \) is their difference with the valley between them being equal to 10% of the peak height. The single focusing magnetic analyzer just described permits resolutions in the range 300 to 1000.

Double Focusing: For a much higher resolving power usually needed in organic stoechiometry.
therefore, be refocused over a wide area, which limits the resolution of the systems employing direction focusing. Considerable increase in resolving power is achieved by elimination of this energy spread in the ion beam before entering the magnetic field. For double focusing the beam is first made to traverse a radial electrostatic field in which it experiences a force given by

\[ Ee = \frac{mv^2}{r} \]  

(Eq 5)

For a given electrostatic field, the radius of curvature of the ion depends only on the energy, and ions of the same mass but different velocity will be separated. The ions are then subjected to magnetic analysis to achieve mass separation. With proper design of components a mass spectrometer containing both an electrostatic sector and a magnetic sector can focus with respect to both velocity divergence and energy divergence. The improved double focus enables entrance and exit slits to be narrowed with a corresponding increase in resolving power to as high as \( \sim 50,000 \). Figs 8 and 9 show two common arrangements used in Nier-Johnson and Mattauch-Herzog double focusing commercial mass spectrometers, respectively. The significance of the high resolution lies not so much in distinguishing large ions differing by unit mass, but in the ability to distinguish small masses differing by a fraction of a mass unit (see below)

**Ion Detection and Recording:** The positive ions separated by the analyzer can be detected and measured by either an electrical detector
or by photographic means. The ion currents are usually in the range of $10^{-8}$ to $10^{-16}$ amp but occasionally currents as low as $1.6 \times 10^{-19}$ amp (1 ion/sec) may have to be measured.

In the conventional electrical detector, the potential drop produced by the ion current across a resistor is measured after amplification by a direct current amplifier or a vibrating reed electrometer. However, most modern instruments for qualitative organic mass spectrometry use an electron multiplier. This remarkable device gives a current amplification of $10^3$ to $10^8$ with very low noise and a high speed response. For quant analysis on the other hand, a current amplifier is still preferred because of its superior stability and invariant gain. The output of either of these detectors is recorded on an oscillograph equipped with three to five galvanometers to provide a wide dynamic range.

Photographic plates have been used since the early days of mass spectrometry for precision mass measurements. Due to its inherently low sensitivity and requirement of auxiliary equipment for data handling, photographic detection has mostly been replaced by electrical methods. Nevertheless, photographic detection is essential in spark source instruments for the analysis of trace impurities in solids because it is an integrating detector, and furthermore, it is insensitive to the high noise associated with the spark source. Details of various detection methods and equipment are available in a number of books (Refs 30 & 64).

**Sample Introduction System:** The general method of electron impact ionization of molecules requires a sample to be in the vapor state at a pressure not exceeding $10^{-4}$ torr. Unless the sample exhibits a slight vapor pressure below its decompn point it cannot be ionized except by special methods like spark source. The function of the sample handling system is, therefore, to vaporize the sample in a heated vacuum system and release it into the ionization source at a controlled rate so as to maintain a low pressure. Gaseous and liq samples are held in a glass or stainless steel reservoir (about 2000ml at 100 microns) served by a vacuum pump and heating oven, and separated from the source by a "gold leak" or a sintered glass leak. While gas samples may easily be expanded into the heated reservoir, liquids are injected thru a silicone rubber diaphragm. Solids, being low in vapor pressure are, however, introduced directly into the source by means of a solid probe. The probe consists of a rod at the end of which is placed a small sample, typically in a glass capillary, and inserted into the ion source thru a vacuum lock.

**Commercial Instruments:** Because of the proliferation of applications of mass spectrometry in organic and analytical chemistry, there are instruments marketed by numerous companies today. Some of the popular ones are the low resolution, single focusing model 21-490 and the high resolution, double focusing models 21-492 and 21-110 of Du Pont de Nemours Co, and the double focusing model MS-9 of Associated Electrical Industries.

**Mass Spectra and Chemical Structure:** While there are a number of books (Refs 16, 30, 49 & 64) already referred to, which deal with details of the instrumentation and techniques of mass spectrometry, there are several concise introductory texts (Refs 10, 21 & 52) on the interpretation of mass spectra. Still other recent books deal comprehensively with organic structural investigation by mass spectrometry. One of these (Ref 63) discusses fundamentals of ion fragmentation mechanisms, while the others (Refs 7, 15, 20, 28 & 29) describe mass spectra of various classes of organic compounds. In the allotted space for this article methods of interpretation of mass spectra and structural identification can not be described in depth. An attempt is, therefore, made only to briefly outline the procedures used in this interpretation.

The first step in the application of mass spectra is obviously to obtain a list of fragment ions formed by electron bombardment of the molecule under study and their relative amounts by appropriate techniques. The goal from this point will necessarily be to relate the positive ions to the molecular structure whether it be an unknown structure to be identified, or a known structure of which a knowledge of fragmentation is desired. The fragment ions observed indicate the pieces of which the molecule is composed.

**Elemental Composition of Ions:** After recognition of the major ions in the spectrum the next step will be to determine their elemental com-
position, partly by "informed" guessing, and partly with the help of isotopic satellite peaks and a calculation of "ring + double bonds". The natural abundance of heavy isotopes of elements, eg, $^{13}$C, $^{15}$N and $^{37}$Cl give associated peaks 1 and 2 amu higher than the normal masses. As an example, in the mass spectrum of naphthalene (C$_{10}$H$_{8}$) the 1.1% natural abundance of $^{13}$C gives rise to a peak at m/e 129 approximately 11% (1.1 x 10) in intensity compared to m/e 128. The "ring + double bonds" calculation is based on the fact that the total number of rings and double bonds in a molecule of the formula C$_{n}$H$_{2n}$N$_{2}$O$_{n}$ will be equal to $x-\frac{1}{2}y+\frac{1}{2}z+1$ because of the valences of the elements involved. In the example of naphthalene this value will be 7 which is equal to 2(rings)+5(double bonds). Presence of several elements can complicate these basic rules, but logical extension of these rules and consideration of several ions in the spectrum will resolve the difficulties (see Ref 63 for details).

The Molecular Ion: The first important piece of information to be derived from the mass spectrum about the compound under study is the molecular weight, and to obtain this the peak corresponding to the molecular ion (M$^+$) must be recognized. For a number of compounds however, the M$^+$ is not sufficiently stable to be present in appreciable abundance. The peak at highest m/e is therefore, not necessarily the M$^+$. Secondly, the molecular ion usually gives several isotopic peaks (P$^+$1, P$^+$2, etc), and the ion of literally highest mass in the spectrum is not the most abundant species. Thirdly, the peak of highest mass may be an artifact caused by an impurity, spectrometer background or an ion-molecule reaction. Further purification, background scans and operation of the instrument at lower sample pressure, respectively, can eliminate this uncertainty. After these initial checks, other criteria (Ref 63) which are "necessary but not sufficient" must be met: a) it must be the ion of highest mass, b) it must be an odd-electron ion (see below), and c) it must be capable of yielding the important ions in the high mass region of the spectrum through loss of logical neutral species (see below). If the ion fails any of these tests, it cannot be the molecular ion; if it passes the tests, it is still possible that it is not the molecular ion. Then, one may resort to obtaining the chemical ionization or field ionization spectrum.

Odd Electron Ions: Ionization of a molecule involves loss of an electron and, therefore, the molecular ion is a radical species. Such an ion with an unpaired electron is called odd electron ion denoted by the symbol, $^\ddagger$. The molecule ion must be an odd electron ion appearing at an even mass unless the molecule contains an odd number of nitrogen atoms. When the odd electron ion decomposes by the loss of a neutral radical species, the resulting ion would then be an even-electron ion. This distinction leads to the important concept of electron "counting" in mass spectral interpretation. This electron "bookkeeping" is very helpful, since the majority of fragmentation reactions are understood in terms of electron shifts governed by the familiar rules of charge stabilization by induction and resonance.

Neutral Loss: Only a limited number of neutral fragments of low mass which are eliminated in decompositions of molecular ions. Examples are H, H$_2$, CH$_3$ and OH. Therefore, the presence of a major ion below the molecular ion at an improbable interval (eg, loss of 4 to 14, 21 to 25 amu) will indicate that the latter is not the molecular ion.

Postulation of Molecular Structures: The postulation of the structure of an unknown molecule is based on several major kinds of general structural information available in the mass spectrum. McLafferty (Ref 63) suggests the following systematic approach:

(a) General appearance of the spectrum: The mass and relative abundance of the molecular ion indicates the size and general stability of the molecule. The number of abundant ions and their distribution in the mass scale are indicative of the type of molecule and the functional groups present. Examples are spectra of aromatic compounds showing low fragmentation and spectra of alkanes with characteristic pattern of even electron ions at 14 amu intervals.

(b) Low Mass Ion Series: Low mass ions indicate general structural features: 1) Series separated by CH$_2$ groups — 15, 29, 43, 57, etc; 2) Homologous series from substituted alkyl group, amines, 30, 44, 58; alcohols, 17, 31, 45, 59, 71; ketones, 43, 57, 71; chloroalkanes, 49, 63, 77; aromatic ion series, 39, 50, 51, 52, 63, 64, 65, 75, 76, 77
(c) **Small Neutral Loss:** Fragment ions of highest mass are the result of the loss of small neutral species which allow simple and positive assignments. For example, the ions at \((M-1)^+\), \((M-15)^+\), \((M-18)^+\) and \((M-20)^+\) almost always represent the loss of \(H\), \(CH_3\), \(H_2O\) and \(HF\), respectively, from the molecular ion

(d) **Characteristic Ions:** The mass of a large ion represents structural information about the ionic species as well as the complementary neutral portion of the molecule. For many particular mass values there are only a few characteristic structural groupings that commonly give rise to the corresponding peaks in the mass spectra. Examples are \(m/e\) 30 from amines, \(m/e\) 74 from methyl alkanoates, \(m/e\) 91 from benzyl substituted compounds, \(m/e\) \((M-27)^+\) from aromatic ethyl esters and \(m/e\) 149 from phthalates

(e) **Probable Structure:** All the information and postulations gathered above must now be utilized to deduce the most logical structure. One should then predict the spectrum from the postulated structure and compare with the unknown spectrum. The elimination of all but one possibility for the molecular structure of course does not prove that this one is correct unless a reference spectrum of this compound can be obtained

Comprehensive correlation tables of various ion series, characteristic fragment ion and neutral fragments from different classes of compounds are available in various sources (Refs 10, 11 & 63). A number of general rules in understanding fragmentation mechanisms and for prediction of prominent peaks in a spectrum are summarized in Refs 10 & 63

**High Resolution Technique:** As indicated earlier, double focusing mass spectrometers are utilized to achieve a high resolving power. The most common application of the high resolving power is the determination of precise empirical formulas of molecular and fragment ions from an exact mass measurement. The basis of this method is that all atoms have non-integer masses on a \(C = 12.0000\) atomic standard, as shown by the examples in Table 2 (Ref 56b). Using these values it can be seen that several combinations of atoms having the same integral mass show a significant difference in their non-integral masses. Beynon (Ref 6a) was one of the first to realize that measurement of the mass of the ion with sufficient accuracy would give an unequivocal identification of its elemental composition. Thus the ion \(C_7H_6O^+\), \(m = 92.0626\) can be distinguished from \(C_7H_8D^+\), \(m = 92.06105\) if a resolving power of 60,000 is used. Fig 10 illustrates a well resolved multiplet at \(m/e\) 260 obtained with a resolving power of \(\sim 20,000\) (Ref 20)

\[
C_{15}H_{16}O^+ \\
(260 \cdot 2026)
\]

\[
C_{16}H_{12}S^+ \\
(260 \cdot 1486)
\]

\[
C_{18}H_{28}O^+ \\
(260 \cdot 2967)
\]

Fig 10 A typical high resolution scan showing the multiplet at mass 260

Another, more reliable and extensively used technique to obtain the exact mass is the "peak matching" method (Refs 7 & 63). Here, instead of slowly varying the magnetic field, a constant magnetic field is used while the accelerating voltage is rapidly changed to bring, alternately, a reference ion and an unknown ion into focus at the collector slit. Eq 3 shows that the ratio of the voltages under these conditions leads to the ratio of the masses. Thus, the ratio required to superimpose the two peaks on the oscilloscope is measured, and the mass accuracy (2 to 5 ppm) attained with this method is 10 to 100 times the resolving power of the instrument (Ref 63)
Table 2  Exact Nuclidic Masses

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</tbody>
</table>

Computer Techniques: McLafferty (Ref 63) has pointed out that the usefulness of elemental composition information increases exponentially with increasing mass, since the number of elemental combinations with the same integral mass becomes larger. There are compilations of exact masses and elemental compositions available (Refs 12a, 13 & 18a). Spectral interpretation will be simplified in important ways if elemental compositions of all but the smallest peaks are determined. Deriving the elemental compositions of several peaks in a spectrum is extremely laborious and time-consuming. However, with the availability of digital computers such tasks are readily performed. A modern data acquisition and reduction system with a dedicated online computer can determine peak centroids and areas for all peaks, locate reference peaks, interpolate between them to determine the exact masses of the unknown peaks, and find within minutes elemental compositions of all ions in a spectrum (Refs 28b & 28c).

- In recent years a variety of computer systems and programs have been developed to process and present data in a readily interpretable form (Refs 18b, 28b, 28c, 56c & 77). Detailed accounts of these computer applications are available in the literature (Refs 18b, 28b, 28c, 49, 52, 56c, 63, 64 & 77). Available programs include those which can perform spectral interpretation at various levels (Refs 28a, 39a, 49a, 52a, 52b, 52c, 56d & 65a) and those designed for matching an unknown spectrum against a file of reference spectra and retrieval of closely similar spectra (Ref 78). Even if the unknown spectrum is not on file, valuable structural information can be gained from the located spectra.

Combined Gas Chromatography and Mass Spectrometry: Combining a gas chromatograph (GC) with mass spectrometer (MS) has given rise to one of the most powerful tools in instrumental analysis today. Gas chromatography has long been known to be an excellent means to separate the constituents of a mixture, while the mass spectrometer is unique in its specificity, sensitivity and content of structural information. A tandem arrangement of the devices (Ref 28d), therefore, had presented an obvious attraction and a challenge to the chemist. The eluted fractions from a GC may be collected by a cold trap or an adsorptive trap and later introduced into the inlet system of a mass spectrometer for analysis. A logical improvement on this is the direct coupling of the two instruments using an "interface" designed to remove most of the

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![Diagram of GC-MS instrument](image-url)

**Fig 11** A general block diagram of GC-MS instrument
Fig 12 Flame ionization detector chromatogram of methyl esters of a naturally occurring acidic extract

Fig 12a Plot of total ionization (ordinate) vs mass spectrum index number corresponding to chromatogram (a) above
carrier gas and enrich the sample (Refs 30, 49 & 64). A stream splitter at the exit end of the column diverts a portion of effluent to a normal GC detector and the rest passes thru an enrichment device of which there are several types (Refs 30, 49 & 64). As each GC peak emerges a quick mass spectral scan can be taken for its identification. Unresolved or poorly resolved peaks are, however, troublesome to deal with by manual scanning. Digital computers again provide an obvious answer to this problem (Ref 28d). In fact, digital computers have become indispensable in handling complex chromatograms comprising numerous peaks encountered commonly in biochemical, clinical, ecological and forensic samples which contain a formidable wealth of information (Refs 30, 49 & 64). The modern GCMS system, therefore, almost always employs a fast, automatic, repetitive scanning of mass spectrometer in combination with an on-line computer and data reduction system. Fig 11 shows a block diagram of GCMS system (Ref 49). With this system literally hundreds of peaks that might emerge from a GC in a short time can be efficiently scanned by the mass spectrometer, the scan information stored and presented later in three basic forms: (Refs 49 & 64): a) a plot of total ion current with time which represents the GC profile; b) plot a "mass chromatogram" which traces a few selected ion masses running thru the chromatogram, and c) print partial or complete mass spectrum from a selected scan (Refs 49 & 64). Figs 12 & 12a (Ref 28d) illustrate a typical flame ionization detector chromatogram and the corresponding total ion current trace reconstructed by computer. Detailed descriptions of GCMS data systems and their applications are available in a number of reviews (Refs 45a, 65b & 79) and books (Refs 30, 49 & 64).

Compilations of Reference Spectra: There are several compilations of reference mass spectra available of which the oldest is the American Petroleum Institute (Ref 82) collection of spectra obtained mostly on the older type instruments. Recent collections index spectra variously, eg, under reference number (Ref 19), molecular weight (Refs 12 & 19), molecular formula (Ref 19), fragment ion values (Ref 19), and base peak (Refs 12 & 19). A quarterly journal, "Archives of Mass Spectral Data" (Ref 32) is devoted to publishing new spectra, and in addition there are a few private collections of uncertified spectra (Refs 80, 81 & 83). In structural elucidation work, the eight largest peaks in a mass spectrum need to be used for reference purposes. The "Eight Peak Index Mass Spectra" (Refs 12, 19, 32 & 43) are of this type. The most recent exhaustive collection appears to be "Registry of Mass Spectral Data" (Ref 74) consisting of some 19,000 bar-graph spectra, arranged according to the exact molecular weight and structure of compound.

Mass Spectral Studies of Explosives and Related Compounds: The earliest mass spectral investigations of interest to expls and propnts were by Collin (Refs 2, 3 & 4) who studied the major ions, dissociation processes and appearance potentials of a series of nitrate esters, nitroparaffins and nitrosoamines. Mass spectra of many more nitro compounds which include nitro alkanes, nitrate esters, and nitro esters were next reported by Boschan and Smith (Ref 6). Mechanistic studies of the fragmentation of nitro alkanes (Refs 17 & 18), nitrate esters (Ref 33) and nitro aromatic compounds (Ref 14) were also made and later summarized in Ref 15, ch 16. Contrasting fragmentation pathways of mono and polynitro aliphatic compounds in the series \( \text{C}(\text{NO}_2)_x(\text{CH}_3)_4x \), \( x = 4 \) to 0 and \( \text{C}_2(\text{NO}_2)_x(\text{CH}_3)_6x \), \( x = 6, 4, 2 \) - were investigated as a function of \( x \) by Larkin et al (Ref 38). In another series of papers by Meyerson and coworkers (Refs 24, 26, 53 & 54), electron impact fragmentation of isomeric nitrotoluene, nitro biphenyls and trinitrobenzene were studied using high resolution, metastable scanning and variable ionizing voltage techniques.

Mass spectra of the important explosives RDX, HMX, TNT, TNB and Tetryl were first briefly reported by Meyer (Ref 34) and later investigated in greater detail with high resolution and \( ^{15}\text{N} \) labeling techniques by Bulusu et al (Ref 45). Mass spectrometric studies of the photodecomposition of \( ^{15}\text{N} \) labeled dimethyl-nitramine (Ref 56) and the thermal decomposition of HMX and RDX (Refs 27 & 31) illustrate the application of these techniques to studies of reaction mechanism and bond dissociation processes. Nitroguanidines have only recently been investigated by Beynon (Ref 35).
Analytical applications: Mass spectrometry has been applied to a variety of analytical problems related to explosives, some of which have already been mentioned. Identification of the principal constituents of explosives has been attempted from electron impact cracking patterns (Refs 34, 35 & 38), as well as chemical ionization spectra (Refs 69, 70 & 71). Such methods necessarily include vapor species analysis and are directed to detection of buried mines (Refs 69, 70 & 71) and forensic applications (Ref 69, 70 & 71). The vapor species may include unchanged explosives (Ref 72) themselves or products of thermal decomposition and explosions. Kinetic studies (Refs 25 & 39) of the thermal decomposition of HMX and RDX were aided by quantitative mass spectrometric analysis. Mass spectrometry was also applied to the analysis of the decomp gases from delay powders, M2, M15 and M17 propellants (Ref 5a). More recently, an application of a gas chromatography/mass spectrometry method to the analysis of exhaust gases from the XM-19 rifle was described (Ref 59). Use of spark source mass spectrometry to trace elemental analysis of explosives (Refs 68 & 75) has already been referred to.

Written by: S. BULUSU


Masuritas. Coal mining, low freezing expls, manufd from 1903-11 by Masurite Explosives Co of Youngstown, Ohio. They consisted essentially of Amber nitrile (up to 93%) and waste oils from paint factories, together with certain chemicals to sensitize the mix.

Refs: 1) W.H. Blumenstein, CA 5, 2949 (1911) 2) Van Gelder & Schlatter (1927), 702

Matagnites. Expls fabricated in the village of Matagne-la-Grande, Belg, from which the name was derived: (1) Blasting Matagnite or Detonating Matagnite contd NC to which was added NG and/or NB in such quantities that no exudation took place; (2) Gelatin Matagnite contd the above ingredients plus sawdust and inorganic nitrates

Refs: Daniel (1902), 419

Matanzette. Swiss Dynamite invented about 1877 contg NG 40% plus sand, ochre, powd coal and resinous materials (Ref 1). Ref 2 describes it as a mixt of NG, sand and chalk

Refs: 1) Daniel (1902), 419 2) CondChemDict (1942), 290

Match. In lay language a match may be defined as “an instantaneous fire producer consisting of a short stem, rod, or tube, tipped at one or both ends with a compn or paste, inflammable by friction, or when brought into contact with a chemical reag”. The term is also applied in military and mining jargon to “a cord or thread impregnated with combustible material capable of burning along its entire length, in order to convey fire from one point to another, not ignitable by friction” (Ref 3)

The history and development of commercial and military matches are covered in Refs 1, 2, 3,
4 and 8. Present friction type matches may be divided into “non-safety”, or strike anywhere matches, and “safety” matches, which are supposed to ignite only when rubbed on a prepared surface.

A safety match head is, essentially, K clorlate in a matrix of animal glue. The striking strip is composed of red P in a similar binder. Use of additives and adjustments in the mfr process results in a safety match which ignites easily when rubbed on the striking surface. The friction and contact of K clorlate crystals with red P results in the ignition of the match head which, in turn, causes the ignition of paraffin impregnated in the match splint.

Typical safety match head and striker compns are given in Tables 1 & 2 (Ref 8).

### Table 1
**Commercial Safety Match Head Composition, %**

<table>
<thead>
<tr>
<th>Component</th>
<th>Tip</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal Glue (Hide) Glue</td>
<td>9–11</td>
<td></td>
</tr>
<tr>
<td>Extender (Starch, Dextrin)</td>
<td>2–3</td>
<td></td>
</tr>
<tr>
<td>Sulfur (Rosin)</td>
<td>3–5</td>
<td></td>
</tr>
<tr>
<td>Potassium Chlorate</td>
<td>45–55</td>
<td></td>
</tr>
<tr>
<td>Neutralizer (Zinc Oxide, Calcium Carbonate)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Infusorial (Diatomaceous) Earth</td>
<td>5–6</td>
<td></td>
</tr>
<tr>
<td>Other Siliceous Filler</td>
<td>15–32</td>
<td></td>
</tr>
<tr>
<td>Burning Rate Catalyst (Potassium Dichromate or Lead Thiosulfate)</td>
<td>to suit</td>
<td>to suit</td>
</tr>
<tr>
<td>Water-Soluble Dye</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2
**Safety Match Striker Compositions, %**

<table>
<thead>
<tr>
<th>Component</th>
<th>Tip</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal Glue</td>
<td>16</td>
<td>9.3</td>
</tr>
<tr>
<td>Dextrin</td>
<td>20</td>
<td>7.0</td>
</tr>
<tr>
<td>Red Phosphorus</td>
<td>50</td>
<td>37.2</td>
</tr>
<tr>
<td>Antimony Sulfide</td>
<td>—</td>
<td>33.5</td>
</tr>
<tr>
<td>Iron Oxide (Fe$_3$O$_4$)</td>
<td>—</td>
<td>7.0</td>
</tr>
<tr>
<td>Manganese Dioxide</td>
<td>—</td>
<td>3.4</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>5</td>
<td>2.0</td>
</tr>
<tr>
<td>Powdered Glass</td>
<td>25</td>
<td>0.6</td>
</tr>
<tr>
<td>Sand</td>
<td>30</td>
<td>—</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>4</td>
<td>—</td>
</tr>
</tbody>
</table>

A variation of the regular match is the pull-match, a version of which is the M Friction-Type Fuze Lighter (Ref 5), in which the traditional role of striker and match is reversed. The match mixt is located in a metal cup, and a length of wire, corrugated and covered with striking mixt near the end, is threaded thru a hole in the cup, with a handle for pulling the wire thru it. The match cup is enclosed in a length of stiff paper tubing for insertion of a delay fuse, held in a fixed position in the tube by a metal ferrule with sharp protrusions. On removal of the wire with a fast pull, the device reliably produces a spit of flame within the tube and transfer of the fire to the fuse train.

Quickmatch, a type of BlkPdr fuse is used for conveying fire to the combustible portion of pyrotechnic devices. It was formerly used for igniting charges in both military and civilian blasting. A match is distinguished from a fuse in that it conveys fire nearly instantaneously, whereas a fuse conveys the fire at a comparatively slow, reproducible rate. Quickmatch (Ref 7) consists of cotton strands impregnated with BlkPdr mixed with starch paste. Mealed (Class A) quickmatch contains additional fine BlkPdr as a coating, which increases the burning rate. Of the three types described in the Military Specification (Ref 7), Type III is intertwined with annealed copper wire. Their burning
Electric matches (Ref 6) are small resin-impregnated paper strips on which conductive brass strips are laminated with a wire loop affixed over one end. Two layers of K chlorate, Pb mononitro resorcinale, and NC priming material are followed by a chlorate, charcoal, lacquer mix for flame and fire transfer, and protective coatings of clear lacquer form a bulb resembling a book-match tip. Ignition is achieved by a current of 500mA for a minimum of 50ms. This is one example of a series of electric matches which are manifold to various current input requirements with different chemical compositions.

Written by: S. M. KAYE


Matchlock. A small arm invented toward the end of the 14th century which represented the first attempt at automatic ignition. The device consisted of a long hammer, pivoted in the gun stock, which held a piece of slow match. When the trigger was pulled, it pressed the burning match down until it touched the powd in the pan, and thus fired the weapon. A serious defect in the matchlock design was the vulnerability of the match to moisture, resulting in non-function under rainy conditions. The matchlock was superseded by the flintlock at the end of the 17th century

Ref: Balleison (1945), 3

Materials Handling in Ammunition Plants.

Materials handling applications can be made wherever materials are transported, positioned, or stored, the most extensive use being in manufg. Manufg involves elements of motion, time, quantity, and space: motion to transport materials between work stations, time to process and handle materials, quantity to establish work schedules and material flow rates, and space to house materials, machines, and employees. The optimum manufg system is one designed to achieve the best possible integration of these elements relative to the desired goals of the manufacturer (Ref 4)

Material handling equipment should be selected as part of an integrated manufg-systems design. Factors that enter into equipment selection include (1) what material is to be handled, (2) where the material is to be moved, positioned, or stored, (3) when the material is to be moved in the manufg cycle, (4) how reliable the equipment types to be employed are, (5) whether projected mechanization costs can be justified, and (6) whether the handling system design will permit the types of controls desired by management (Ref 5, p 1054-R)

The productive system may incorporate several different types of materials handling equipment. One basis for classification is by use: eg, transporting equipment, positioning equipment, and storage equipment. Then there are subdivisions, eg, transporting equipment may follow a fixed path or permit movement within an area; positioning equipment may or may not include small storage capacities, and storage equipment may be either fixed or portable.

Transporting equipment includes conveyors, monorails, hoists and cranes, industrial trucks, and air-float platforms. Highway trucks, ships, rail cars, and aircraft are excluded. Conveyors, monorails, and certain types of hoists and cranes provide fixed-path movement of materials; other crane types, industrial trucks, and air-float platforms provide for area coverage. Positioning equipment includes parts-handling equipment that is employed at individual work stations. The goals in employing such mechanized loading and unloading equipment are to increase the rate of production, provide greater operator safety, improve product quality, improve cutting tool life on machine tools, ease the handling of hot, fragile, or clean parts, and reduce operator fatigue. The major types of positioners are levelers, strip and coil feeds, bar transfer, mechanical transfer arms, dial feeds, magazines and parts selections. Storage equipment includes all types of containers, racks and accessories used to store material (Ref 5, pp 1055–58)

Materials handling in ammo plants, of course, involves unique considerations and constraints relative to personnel safety and the preservation of facilities. These are reflected in limita-
tions on the quantities of material handled in one site or area, scrupulous attention to the elimination of such potential sources of material initiation as impact, friction, electrostatic charge accumulation, etc., extensive use of remotely controlled operations wherever feasible, adequate shielding or barricading of hazardous processing procedures and the structures housing them, and storage areas so spaced that initiation of one will not result in a chain reaction.

Modern materials handling techniques in US Army Ammunition Plants are detailed in the Refs given under Modernization Engineering Project for US Army Ammunition Plants in this Vol. A study of materials handling at the Louisiana Army Ammunition Plant, carried out under the above project, is reported in Ref 6. The principal objectives of this study were to develop recommendations to modernize materials handling in a cost effective and safe manner. It was reported that efficient materials handling at LAP (load, assembly and pack) plants was constrained by a number of factors that presently exist. These factors include old facilities that do not have adequate access and docks. At many production lines there is not adequate on-line storage, so materials must be double handled by being stored initially in off-line warehouses. The present inventory control system also encourages double handling, as do the warranties that are provided by component vendors. Safety rules also limit the storage of efficient quantities of exps. Recommendations made included a high-rise, automated, random access warehouse for inert materials; a centralized magazine facility for receiving, pre-processing and the temporary storage of bulk exps; barricaded holding yards for the temporary storage of containerized finished ammo; an automated rail transportation system; magazine modernization; new on-line warehouses; new conveyors; and a new manual tow tractor system.

Other material handling studies at the Kansas, Lone Star and Longhorn Army Ammunition Plants are detailed in Refs 2, 3, 7 & 8.

Written by: S. M. KAYE


Materials of Construction in Ammunition Plants. Over the last 60 years criteria and methods based upon results of catastrophic events have been used for the design of expl facilities. The criteria and methods did not include a detailed or reliable quantitative basis for assessing the degree of protection afforded by the protective facility. Recently, extensive research and development programs have been undertaken to establish procedures which permit a more sound and scientifically based approach to current and future design requirements (Refs 1 to 9)

Modern methods for the manuf and storage of expl materials, which include many exotic chemicals, fuels, and propelants, allow less space for a given quantity of expl material than previously permitted. Such concns of expls increase the possibility of the propagation of accidental explosions (one accidental explosion causing the detonation of other expl materials). It was evident that a requirement for more accurate design techniques had become essential. Ref 3 describes a rational design method to provide the required structural protection. It presents methods of design for protective construction used in facilities for the manuf, maintenance, modification, inspection, and storage of expl
materials. Its primary objectives are to establish design procedures and construction techniques whereby propagation of explosions (from one bldg or part of a bldg to another), or mass detonations will be prevented and protection for personnel and valuable equipment provided. Secondary objectives include (1) to establish blast load parameters required for design of protective structures, (2) to provide methods for calculating the dynamic response of reinforced concrete and other materials, (3) to establish construction criteria necessary to afford the required strength to resist the applied blast loads, and (4) to establish guide lines for siting expl facilities to obtain max cost effectiveness in both site planning and structural arrangement, providing closures, and preventing damage to interior portions of structures caused by structural motion and shock.

The design method described in Ref 3 accounts for the close-in effects of a detonation, including associated high press and nonuniformity of the blast loading on protective structures or barriers. The dynamic response of structures can be calculated, and qualitative and quantitative values are developed to provide the properties necessary to supply the required strength and resilience specified by the design. Although this Ref concentrates on the procedures and techniques required for the design of reinforced concrete protective structures, this does not imply that concrete is the only useful material for protective construction.

In this connection, mention must be made of suppressive panels as an alternative to the conventional laced concrete wall (Fig 1) to protect against the effects of accidental explosions. Suppressible structures are comparatively new and, hence, represent an infant technology as contrasted with concrete barriers. These structures use steel panels made of several layers of louvered and perforated plates, and of angle irons or zee bars. The venting that results from this construction is designed to allow controlled release of blast effects from an explosion within the structure, thereby reducing the resulting external overpressure. At the same time, complete containment of fragments and fire brands, and significant reduction of the fireball can be achieved. Successful tests, both sub-scale and full scale, have been conducted with suppressive structures. Fig 2 shows some of the detail of a structure's panel construction representing one of many panel configurations that have been used. The inner layer is made of angle irons. The next three layers are perforated plates, and the outermost layer is louvered plate. The layers are held together by steel channels (Refs 5, 6, 7, 8 & 10).

See also under Buildings and Other Structures at Ordnance Establishments in Vol 2, B320-R to B321-R, and Barricades in Explosives and Ammunition Installations in Vol 2, B22-R to B23-R.

Written by: S. M. KAYE

Refs: 1) E. Cohen et al, "Establishment of Safety Design for Use in Engineering of Explo-
OPERATIONAL SHIELDING APPLICATION

ENVIRONMENT

REACTION

Fig. 2
Matter Explosives. The following expls were patented by O. Matter of Switz. A plastic dynamite consisting of tar distillates mixed with inorg oxidizers such as nitrate, chlorate or perchlorate (Ref 1). Mixts of nitrates, chlorates or perchlorates with w sol chlorinated hydrocarbons such as chloronaphthalene, benz or tar-dist residues as thickening agents (Ref 2). A carbonaceous material, free from inorg matter and suitable for use in BlkPdr or priming compns, is prep'd by extrg coal with high boiling oil solv such as coal-tar oils, followed by filt and removal of the solv from the filtrate by distn (Ref 3)

Refs: 1) SwissP 220755 (1942) & CA 42, 6538 (1948) 2) SwissP 228653 (1943) 3) SwissP 244352 (1946) & CA 43, 4468 (1949)

Marweed (Mattgrass, Espartograss, Sparte in Fr). One of several species of seaside grass, among which are the Lygeum Spartum or hooded matweed of the Mediterranean and Anophila Arenaria of Holland. The name Esparto is used for the fibers covering coconut shells. The dried weed may be nitrated to give an expl compd (see below)

Nitromatweed (Matweed Nitrate, Nitroparte in Fr). Prepd by nitrat of dried matweed with mixed nitric-sulfuric acids in a manner similar to the prep' of NC. Trench, Faure and MacKie (Ref 2), in 1876, patented expls containing as a base "nitrosparte" (or other nitrated cellulosic material such as cotton, hay, agave, hemp, flax, straw, aloe, yucca, etc) together with resin, ozokerite, collodion, glycyrin, charcoal and soot. Hengst (Ref 3), in 1898, patented a smokeless powd containing "nitroparte" prep'd by nitrat of fibers covering the coconut shell


Mauretta Powder. Contd K nitrate 82.4, K chlorate 0.7, sulfur 0.3, charcoal 7.1 & wood ash 6.5%

Ref: Daniel (1902), 420

Maxim Explosive. Patented in 1885 in Engl. Prepd by mixing lp of compn (K nitrate 74.18, sulfur 14.40 & paraffin 11.42%) with 3ps of regular BlkPdr

Ref: Daniel (1902), 420

Maxim, Hiram Steven, Sir (1840–1916). American expatriate in Engl who specialized in Ord and expls. His major inventions included (1) design and constrn of the modern machine gun (1884–89), (2) gelatiniz of NC using acet, either alone or in mixt with eth or alc (Brit of 1888), (3) addition of an oil, such as castor oil, to a mixt of NC and NG to obtain a slow burning smokeless powd for small cal weapons, (4) prep of smokeless powd in the form of single-perforated rods, plain or with exterior channels running parallel to the long
axis of the rods; such powders burned more uniformly than solid grains, and (5) prep of smokeless powders containing NC, to which were added resinous materials to reduce barrel erosion (BritP of 1900)

Refs: 1) Daniel (1902), 420-23 2) Van Gelder & Schlatter (1927), 778, 779 & 793

Maxim, Hudson (1853–1927). American inventor, brother of Sir Hiram Maxim. His major inventions included (1) Maximite (see below), (2) Maxim-Schüpphaus powd (see in this Vol), (3) initiating compd prep by adding 1p of MF to 1p of a paste contg NG 75–85 and NC (previously distd in a small amt of solv such as acet) 25–15%; after evapn of the solv, the resulting mix was suitable for use in projectiles such as naval torpedoes, where a large amt of initiator was required (BritP of 1894), (4) a proplnt specially designed for use in cannons contg a min amt of volatile solv; 40ps of guncotton and 8–10ps of NC (sol in NG at 38°) were thoroughlyblended with 8ps of NG and acet equal to about 25% by wt of the total mixt; the resultant thick gelatinous mass was passed thru heated rollers several times to reduce the quant of acet to a min; the rolled sheets were then cut to the desired grain size (BritP of 1896), (5) single-base proplnt contg mixt of insol and sol NC (BritP of 1897), (6) aerial torpedoes contg a min amt of metal and a max of expl (BritP of 1897), (7) automatic pistol (BritP of 1897), (8) automatic cannons (BritP of 1897), (9) Motorite (see in this Vol), (10) safety delay fuze, magnetic submarine mine, etc

Refs: 1) Daniel (1902), 421–25 2) Van Gelder & Schlatter (1927), 793

Maximite. According to Daniel (Ref 1), it was an expl proposed by Hudson Maxim at the end of the 19th century for charging aerial torpedoes. It was prepd by blending sol NC 20–30 with NG 80–70%, allowed to harden and then pulverized. 75–80ps were mixed with 25–20ps of insol NC, satd with w, and the resulting wet mass charged into torpedoes

Marshall (Ref 4) states it was introduced soon after 1900 as a filling for shells. It consisted of a mixt of 90ps of PA and 10ps of nitronaphthalene, which melted at comparatively low temps, but tended to form cavities and consequently caused premature explns

According to Newman (Ref 5), Maximite was a proplnt consisting of NC, NG and castor oil, patented in 1889 by Hiram S. Maxim, to operate the machine gun he invented

Maximite was used in armor-piercing projectiles (Panzergrenaten) until 1903 when it was replaced with Amm picrate, known as Explosive D (Refs 2 & 3)


Maxim-Nordenfeldt Powder (M.N.). An old American guncotton powd, gelatinized with et acet

Ref: Thorpe 2, 485 (1917)

Maxim Powder. One of the varieties of smokeless powd invented by Hudson Maxim, contg guncotton 94, NG 5 & castor oil 1%. It was used in the form of either small square flakes or cylinders, 1.64 inches long and 0.5 inch in diam. Other varieties of Maxim powd contd equal parts of NG and guncotton without castor oil

Ref: Van Gelder & Schlatter (1927), 828

Maxim-Schüpphaus Powder. A progressive burning smokeless powd, invented by Hudson Maxim in collaboration with R.D. Schüpphaus. It was the first multiperforated powd grain, earlier powds having been manufd in the form of strips or of solid or single-perforated rods. According to Daniel (Ref 1), there were two varieties of such powds: (1) double-base powd prep by mixing 80ps of insol NC (13.3% N) with 8ps of sol NC (12.0% N) and 12ps of NG at 50° in the presence of 35ps of acet. To this was added 1p of urea (as stabilizer), previously disd in methanol. This powd was less corrosive to gun barrel interiors than Ballistite or Cordite, both of which contd much more NG (BritP of
1895); (2) single-base powder contd 80ps of insol NC, 19.5ps of sol NC and 0.5p of urea, and was manuf'd in the USA by duPont
Refs:  1) Daniel (1902), 425–26  2) Thorpe 2, 458 (1917)  3) Van Gelder & Schlatter (1927), 780 & 793

Maximum Charge (Charge limite in Fr) is the max charge of an expl that can be fired in a coal mine without causing ignition of fire dust and/or coal dust in air
Ref: Marshall 2, 585 (1917)

Mayevskii, N.V. (1823–1892), eminent Russian ballistician and originator of the science of Exterior Ballistics. He was equally known for his work in the field of Interior Ballistics. In 1856 he designed a method of measuring the pressures in various sections of a gun barrel on firing. In 1867 he conducted expts to detn projectile velocity and correlated press with velocity

Mayrhofer Stability Test. A modification of the Bergmann-Junk Test (see Vol 2, B102-R) for testing the stability of NC and propellants. Mayrhofer recommended the use of 20ml of a 2% KI soln instead of w for the quant collection of decomp products. He also tested NG contg proplnts in both dry and sl moist states, and found that while a stable sample behaved in a similar manner whether heated dry or moist, an unstable powd decompd rapidly in the presence of traces of w. Tonegutti (Ref 3) considered this test reliable for ballistites and unreliable for cordites

Mazut or Masutt. Residue of Russian petroleum after distg off benz (1% at 100°, d 0.725 g/cc), gasoline (3% at 120° to 130°, d 0.775 g/cc), and kerosene (27% at 150° to 250°, d 0.83–0.84g/cc). The resulting black, oily residue, resembling crude petroleum in appearance, has a flash pt of about 100° and d 0.878–0.900 g/cc. It was purified by treatment with sulfuric acid. It has been used as a fuel in boilers, locomotives and boats, as well as in some internal comb engines. In the expl industry, its use was confined to some blasting expls, particularly those contg chlorates
Refs:  1) Colver (1918), 61  2) Hackth's (1944), 517  3) Merriam-Webster's (1951), 1518

M.B. Powder (Modified Black Powder). Consisted of BkPdr in which part of the K nitrate was replaced by K perchlorate. The finely pulv. ingredients were preliminarily mixed, as in the prep of BkPdr, and then incorporated together in a steam jacketed pan. The last operation was dangerous and some fires occurred, which were ascribable to friction in the hot, dry caked material. A similar expl was called Roslin Giant Powder
Ref: Marshall 1, 385 (1917)

MC (Poudre). BkPdr used in Fr as propellant for muzzle loading cannons and as a bursting charge in projectiles
Ref: Daniel (1902), 427

MC No 3 Powder. Austrian safety expl (1898) contg Amm nitrate 91.6 and collodion cotton 8.4%
Ref: Daniel (1902), 427

McRoberts Type Incorporating Machine. Brit device for blending expls contg NG. Unlike earlier equipment, it had no bearings inside the mixer, therefore reducing the danger of NG being initiated by friction. It consisted of a flat-bottomed elliptical vessel placed on a platform which could be raised or lowered. The vessel was provided with two vertical, parallel shafts, supported from above by bearings,
which did not touch the bottom of the bowl. Each shaft had two or more horizontal blades, serving as mixers. The arrangement closely resembled the duPont dipper used to nitrate cellulose, except that the bottom of the mixer was flat and coned no opening. The McRoberts machine allowed gelatinization and incorporation to be carried out in the same vessel, thus avoiding transferring the jelly from a gelatinization vessel to a mixing machine, as was usually done in other systems.

In charging the machine, the platform supporting the mixing vessel was lowered so that the mixing arms cleared the top of the vessel. It was loaded with the required ingredients, and then raised. The mixing blades rotated in opposite directions to each other. When incorporation was complete, the vessel was lowered to clear the blades; and the load was discharged by transferring to wooden containers.

Ref: Barnett (1919), 100–01

Meal Powder (Meal Black Powder). The finest granulation of BkPdr procured for military use. It is designated as Class 8 in Ref 4 and has the following formulation requirements: K nitrate 74 plus 1.0 minus 2.0, S 10.4 plus 1.5 minus 1.0, and charcoal 15.6 plus 1.5 minus 1.0. Granulation requirements are a max of 5% retained on a No 100 US Std sieve, and a max of 50% passing thru a No 270 sieve. Modern methods of prep are given in Ref 3.

Historically, it was prepared in a stamp mill by a procedure developed by the National Fireworks Co (Ref 1). This mill consisted of a solid block of granite in which 3 cup-shaped cavities had been cut. The stamps, which operated in the cavities, were fitted at their lower ends with cylindrical wooden blocks cut from a hornbeam tree. The blocks were replaced when worn.

Weingart (Ref 5) gives the details of another older method as follows: Mount a 50 gal wooden barrel on two uprights in such a manner that it can revolve in a horizontal position on centers attached to the heads. To one of the centers, attach a long rod with a pulley, to be operated by remote control either by a water wheel, air or electric motor. Cut a hole in the side of the barrel and provide it with a tightly fitting plug. Place 300 to 500 lead balls, 1 inch in diam, in the barrel, followed by a thoroughly mixed compn of K nitrate (double refined), 15 lbs, willow charcoal, 3 lbs, and sulfur (flour), 2 lbs. Revolve the barrel slowly, by remote control, for at least 500 turns. The longer it is turned, the finer and more uniform will be the powd. Note: Care must be taken that no foreign matter, such as nails, sand, etc., is introduced into the barrel as this might lead to an expln.

Meal powd has been used historically in pyro for ignition and priming purposes (Ref 1), in colored star compns (Refs 1 & 2), and generally in fireworks, rockets, Roman candles and firecrackers (Refs 5 & 6)


Measurement of Acidity or Alkalininity of Explosives. (Measurement of pH value). These tests consist essentially of extrg the sample of expl with w (either cold in the case of liquids such as NG, or hot for solids such as TNT, Tetryl, PA, etc), and detg the acidity of the resulting extr either by titration, colorimetric methods or by means of a pH meter. These tests are described under the individual compds.

Measurement of pH value, Stability Tests by. These tests det the acidity (pH value) of powds which is produced when they are heated for prescribed times and temps (usually 80 to 110°). In the group are the Hansen, Grottanelli and Pavlik tests (qv)

Mechanical Fuze. Any fuze which depends for its arming and functioning on events primarily of a mechanical nature. Fuzes may consist of a combination of mechanical and electronic features. Proximity fuzes may contain a mechanical delayed arming device; mechanical fuzes may be functioned by electrical energy from a piezoelectric element. The classification is dependent upon which features are predominant.

Variations of mechanical fuze are: (a) Mechanical Time Fuze (MTF) which is actuated by a clocklike mechanism preset to the desired time, (b) Mechanical Time and Superquick Fuze which contains an additional device to cause instantaneous activation as a result of impact, (c) Mechanical Time Fuze, Dummy which is an imitation of a mechanical time fuze having the same shape, weight and center of gravity as the fuze, but without expl components, and (d) Mechanical Time Fuze, Training which is an item identical in configuration to a mechanical time fuze, but is designed for use in training procedures associated with assembly and/or disassembly of a weapon.


MEDINA (Methylene dinitramine, N,N-Dinitrotoluenediamine), CH₄N₂O₄, mw 136.17, N NHNO₂ 41.18%; OB to CO₂ 0.0%; wh orthorhombic needles and rods, also CH₂ plates and tablets from et dichloride: iso-Pr alc 9:1 (Ref 18); mp 105-06° NHNO₂ (Ref 1), 104° (Ref 2), 103.5-4.5 (Ref 11, p 21); CA Registry No 14186-44-6

MEDINA in an acronym for Methylene DINTrAmine. In earlier literature it was called MEDNA (Ref 2), the latter name later used for the isomeric compd methylenedinitritramine which was obtained by the action of nitric oxide on acet (Beil 1, 592) (See under MEDNA in this Vol). This name should also not be confused with MeEDNA, which is N-Methylethylene dinitramine (Ref 2a and see under MeEDNA in this Vol).

Historical. MEDINA was first isolated as a degradation prod from the nitrolysis of hexamine (WWII work done at the Univ of Bristol, cited in Ref 5). It was prep by the hydrolysis of PCX (qv) in boiling et alc and isolated as the Ba salt (Ref 4); and by the hydrolysis of N,N'-DiacetylMEDINA with aq ammonia, yield 25% (Ref 5).

Best Preparation on a Laboratory and Commercial Scale. A. Methylenediformamide. In a 2L round bottom 1 neck flask are placed 540g of formamide and 70g of hexamine. The flask is fitted with a wide bore air condenser topped with a w jacketed reflux condenser, and the flask held at 140° for 5 hours. It is chilled in ice, the solid filtered, and washed on the filter with 90g of formamide. The crude prod may be used in the next step. For a pure sample; the crude solid is dissolved in et alc, decolorized with charcoal, and the soln chilled, mp 142-43°.

B. Methylene(dinitroformamide). Abs nitric acid (19ml) is added dropwise with stirring to a suspension of 5g of crude methylenediformamide in 19ml of acet anhyd at 10-15° degrees; the soln held 2 hours at 0°, poured into 150ml of ice and w with stirring, the ppt filtered, washed twice by slurring with ice w, pressed dry on the filter, and dissolved in 30ml of et acet. The soln is sep from w, dried over anhyd Na sulfate, conced in vacuum, 10ml of iso-Pr alc added, and the prod collected. The methylene di(nitroformamide) is purified by recryst from acet/iso-Pr alc/Skellysolve B or from boiling et chloride, mp 87.0-7.5°.

C. MEDINA. The crude methylenedinitroformamide is pressed dry on the filter, stirred into 105ml of formic acid, and the paste allowed to stand overnight. The next day the soln is filtered thru an acid-proof flt, the formic acid and w removed by codistn with xylene, and the crude MEDINA, which seps as a sand, filtered and dried over paraffin and NaOH in a vacuum; yield 80-100% based on methylene diformamide, mp 98-103°. The crude MEDINA is recryst from 2-nitropropane or et chloride:iso-Pr alc 9:1, mp 104-05° (Ref 11, p 54). This prep is also covered in Ref 20.
Other preparations and isolations. If damp methylenedinitroformamide is allowed to stand for several days, the odor of formic acid is noticed, and MEDINA can be isolated from the residue (Ref 11, p 14). The details of scale-up to 150 lb batches, including exp details and flow sheets, and further scale-up with the aim of prodn of 1000 lbs are given. The report describes a fume-off and fire which occurred during the 53rd run. The cause was attributed to a stuck valve which allowed nitric acid to build up in the reactor (Ref 13, p 57). In Ref 16, p 73 there are cost analysis data for pilot plant and large scale prodn, flow sheet for a proposed coml plant, and material balances. The action of acct anhrd on N,N'-bis(hydroxymethyl)MEDINA regenerates MEDINA (Ref 6); the diNa salt of N,N,N'-trinitromethylene-diamine, on warming with me alc, ppts the Na salt of MEDINA.

Properties. Two cryst modifications are known: I formed from soln and II formed from the melt and is unstable with respect to I (Ref 11, p 23). Photographs and crystal angles of a single cryst of MEDINA I are given in Refs 11, p 25; & 18. Phase diagrams for mixts of MEDINA with RDX, TNT, EDNA, and PA are given in in Ref 11, p 26. Optical props of single crysts of MEDINA are given as nα 1.572, nβ 1.564, nγ 1.598 (Ref 13, p 76). X-ray diffraction patterns of powd MEDINA are given in Ref 13; addnl phase diagrams are given in Ref 13 for mixts of MEDINA with HMX, PETN, BTNEU, Tetryl, Stphnic Acid, and 2,4-Dinitrophenol; ternary diagrams for PA:TNT:ME-DINA and PA:PETN:MEDINA are also given. MEDINA behaves in acq soln as a dibasic acid, forming well-defined salts with alkali and alkaline earth ions (for reactions involving the Ba and Na salts, see above). Similarly are formed salts with 2 moles of methylamine (mp 120° decompn), cyclohexylamine (mp 99–100° decompn), and benzylamine (mp 112° decompn) (Ref 7). The addn of 2 moles of hydrazine in iso-Pr alc to 1 of MEDINA in the same solv gives the fairly stable 2:1 hydrazine salt, mp 126° decompn, Q 2446 kcal/kg, power 148% TNT (Trauzl), 143% TNT (ballistic mortar) (Ref 13). The Ba salt is pptd by addn of Ba chloride soln to solns of MEDINA (it can be regenerated by the addn of HCl to the Ba salt); this salt is used in isola-
tion proc for obtaining high-purity MEDINA (Ref 5). By heating in w to 70° MEDINA is decompd quany into formaldehyde and nitrous oxide, the vel of this decompn varies strongly and in a complicated way with pH (Ref 8). It is presumed to occur by hydration to formalde-
hyde and Nitramide, which decomp into w and nitrous oxide, the kinetics is discussed at length in Ref 16. In the solid phase or concd solns the decomp takes a different course to give a high melting polymer insoluble in most solvs (Ref 11, p 29). The action of 2N aq ammonia gives a small amt of DNPT (Encycl, Vol 5, E91-R), and the mono-amn salt, when allowed to stand with aq formaldehyde gives the same compd (Ref 8). The action of Amm Nitrate in acet anhrd & acet ac gives a small amt of RDX and a very small amt of 1,5-diacetoxy-2,4-di-
nitrazapentane (Ref 3). The addn of MEDINA improves the yield of HMX from the reaction of para-formaldehyde with Amm Nitrate in acet anhrd & acet ac (Ref 3). Similarly, the addn of MEDINA to hexamine nitration mixts raises the yield of RDX from 82 to 145% based on 1 mole of RDX from 1 mole of hexamine (Ref 26); a plausible mechanism is given. A soln of MEDINA in w or acet ac is treated with formalde-
hyde, then concd nitric acid to give 1,5-dinitroxy-2,4-dinitrazapentane, mp 105–06° which is not stable on long storage (Ref 11, p 38). The action of formaldehyde alone gives 2,4-
nitrazia-1,5-pentanediol (Ref 11). The action of acet anhrd & Na acetate at 95° gives a small amt of 1,5-dinitroxy-2,4-dinitrazapentane and an amor solid C₁₁H₂₄N₁₅O₁₆ which decomp bew 280 and 315° (Ref 3). MEDINA gives with formaldehyde in pyridine a compd C₁₂H₁₂N₉O₁₀ (Ref 3). The action of ammonia in eth on a soln of MEDINA in eth ac which has been satd with formaldehyde gives 1,3-
dinitrotrimethylenetriamine, isolated as the N-acetyl deriv (code name TAX), mp 156° (de-
compn) (Ref 7). The reaction of MEDINA in 40% aq formaldehyde with 40% methylamine in eth ac gives 1,3-dinitro-5-methyltrimethylenetriamine, mp 100–04° (decompn). Similarly prepd were the benzyl (mp 127–30° decompn), cyclohexyl (mp 101–02° decompn), and ethyl derivs (mp 88–89° decompn) (Ref 7). A soln of MEDINA in eth acet is satd with formaldehyde, the soln cooled to 0°, and the rosettes filtered
to give N,N'-Bis(hydroxymethyl)methylene di- 
trinitramine, mp 70–75° (decomp) (Ref 6); the 
Can workers were unable to isolate a definite 
prod from this reaction (Ref 3) (See Encycl. 
Vol B, D1356). A compd, mp 122°, was 
isolated when MEDINA was allowed to stand in 
the presence of acid, or not completely freed of 
acid during prep; from IR and other data it 
appeared to be N-hydroxymethylmethylene di- 
trinitramine, but its structure was not rigorously 
established (Ref 11, p 29). MEDINA, primary 
amines, and formaldehyde give hexahydrotria- 
zines contg 2 nitro groups and 1 alkyl group, or 
1 nitro group and 2 alkyl groups, depending on 
reactant ratios (Refs 6, 7, 21 & 24). A similar 
reaction with aliphatic diamines is reported in 
Ref 19, the prods isolated are bicyclic compds 
of the type:

\[
\begin{align*}
\text{CH}_2 & \text{N} - (\text{CH}_2)_n \\
\text{O}_2\text{N} & \text{CH}_2 \\
\text{CH}_2 & \text{N} - \text{CH}_2
\end{align*}
\]

The Na salt of MEDINA was fluorinated in w, 
the soln extd with methylene chloride, and the 
solv evapd to give a yellow oil whose IR spec- 
trum showed absence of NH and the presence of 
NF absorption, and analysis indicated was a 
mixt (Ref 22). Nitramines in the presence of 
sulfuric acid are capable of nitrating reactive 
aromatic compds, but when acetanilide was 
treated with MEDINA in the presence of this 
acid, no nitroacetanilide was isolated. Instead 
compds indicating that the MEDINA had been 
fragmented and the fragments reacted with the 
acetanilide were isolated (Ref 12)

**Solubility.** No quant data in the literature. 
In Ref 11, p 19 the order of decreasing solv is 
given as w, ketones, alcohols, esters, organic acids, 
aliphatic nitro comds, ethers, chlorinated hy- 
drocarnons, hydrocarbons. Within each class the 
solubility decreases with increasing chain 
length

**Spectral properties.** The UV spectra of 
MEDINA and the Traube compd (MEDINA) in 
et alc, acid, and base are compared in Ref 4. 
The peaks for MEDINA are similar in all three 
sols, but the MEDINA peak is shifted from 2600 
to ca 2200 Å in N HCl. The IR spectrum in 
minal oil is given in Ref 21a; the IR spectra of 
MEDINA from different sources are compared 
and appear to be almost identical. The IR 
spectra of MEDINA and decompn prods are 
given in Ref 16, p 59. The NMR is given as: 
chem shifts N-proton 13.1, C-proton 5.10 ppm 
(Ref 27)

**Analytical.** The thin layer chromatog 
of MEDINA and the sepn from other exps and 
nitrarnines on thin layer plates (MEDINA spots 
tend to comet) are described in Ref 23

**Explosion temperature test.** 300–330° in 
5 secs (RDX 260°) (Ref 13)

**Friction pendulum test.** Steel shoe explodes; 
fnre shoe unaffected (Ref 13)

**Heat of combustion.** −230.3 kcal/mole (Ref 
11, p 1); −216.85 ± 0.32 kcal/mole at 25° 
(Ref 15)

**Heat of formation.** −13.84 kcal/mole 
(Ref 15)

**Heat of fusion.** The Q_fusion of mixts of 
MEDINA with PETN, HMX, TNT, RDX, 
BTNEU, EDNA, Styphnic Acid, PA, & Tetryl 
are given in Ref 13, p 97

**Heat test at 80°.** 1.13–3.89% wt loss after 
72 hours (Ref 11, p 30)

**Heat test at 85°.** 2.77–6.54% wt loss after 
72 hours (Ref 11, p 30)

**Hygroscopicity.** No wt gain to 90% RH at 
30° (Ref 13, p 424)

**Impact sensitivity.** PA app 10–11 inches 
(18.3mg sample) vs 8 for RDX, hydrazine salt 
15 inches (11mg sample); BM app 14–21cm vs 
70–100+ for RDX and 100+ for TNT, hydrazine 
salt 92cm (Ref 13), also in this Ref are listed the 
impact sensy of 8 samples of MEDINA 
coated with wax (15–31cm)

**International Heat Test @ 75°.** 0.66% wt loss 
after 4 hours, 1.47–2.24% after 72 hours; the 
effect of many addtives & recrystn solv on 
stability are given in Ref 13. PA seems to be 
the best stabilizer, it is covered in C.W. Sauer, 
USP 2786078 (1957) & CA 61, 9163 (1957)

**Power.** It is reported to have the highest 
expl power of all pure compds tested to date 
(Ref 13, p 423); Ballistic Mortar, 19% of TNT 
(Ref 11, p 1); Trauzl test, 681–727cc (10g 
sample); spherical-lead block test, 568–76cc 
(10g sample) (Ref 11, p 1). Power by spherical 
lead block test of 14 formulations contg ME- 
DINA as well as formulations contg varying propor- 
tions of TNT, MEDINA, and Al are reported 
in Ref 16
Sand test. 71.9g of sand are crushed (RDX 58–61g) (Ref 13).

Toxicity. MEDINA is apparently non-toxic to rabbit penile mucosa; its cumulative effect on abraded and intact rabbit skin is slightly greater than Tetryl; no damage was observed to rabbit cornea; and there was no evidence of sensitization by subcutaneous injection in guinea pigs. It was concluded that its toxicity is similar to that of Tetryl (Ref 11, p 138).

Vacuum stability. Gas evolution was 1.92 mg/g/40 hours (material recrystall twice from et chloride/iso-Pr alc 9:1); 0.89–0.98ml/g/40 hours (sample dried at 40°C in vacuum) (Ref 11, p 30). Another stability test, developed by W.C. McCrone of ARF, consists of following the behavior of crystals of the compound on a hot stage microscope at temps close to the mp. The most stable samples of MEDINA were found to be those recryst from et chloride/iso-Pr alc; the least were prepd by vacuum evap (Ref 11, p 30).

Velocity of detonation. 8700m/sec (Ref 14), deton vel of 7 formulations cong MEDINA are measured and plotted in Ref 16.

Uses. Screening tests showed MEDINA to be 5–10% more powerful than RDX (Ref 16). Several formulations of MEDINA, TNT, & Al were tested as air-blast expls, and some were found to be slightly superior to H-6 (RDX: TNT:Al:wax 47:31:22:5). Three MEDINA-contg formulations were compared with std expls in plate dent, air blast, underwater blast, and frag tests. MEDINA showed a 4% improvement over RDX in shaped charge penetration (Ref 14). MEDINA was tested as a detonator fill, but was unsatisfactory due to poor stability (Ref 14).

Written by: C. H. McDonnell


MEDINA (METHYLENEDIISONITROSOAMINE, or N,N'-DINITROSOMETHANEDIHYDROXYLAMINE) and Salts.

MEDINA is an acronym for MEthyleneDi-isonitrosamine (erroneously called methylenedinitramine in Blatt, OSRD 1944 (1944) (see MEDINA
in this Vol); structure (HON)$_2$CH$_2$,

NO

mw 136.07, N 41.18%; the free acid is unstable and is known only in salts (Refs 2 & 3)

**Historical.** The Na salt was first isolated by the reaction of nitric oxide on acet (Ref 2); later the same worker found that the action of nitric oxide and Na hydroxide on any compd contg the acetyl group would give Na MEDNA (compd treated were mesityl oxide, methyleneisopropyl ketone, acetophenone, and ethyl dimethylacetacetate (Ref 3)); still later it was found that MEDNA salts could be obtained by prolonged contact of nitric oxide with Na ethoxide or K ethoxide (Ref 4). The Ba salt was obtained by the action of nitric oxide on Na isopropoxide or Na 1-phenylethylene oxide followed by the addn of Ba chloride soln (Ref 6). The UV spectra were used to distinguish between salts of MEDNA and MEDINA and to prove the structure of each (Ref 8)

**Salts. Monoammonium.** UV spectra in N HCl at max 231 nm, log $E_m$ 4.10; in w 254 nm, log $E_m$ 4.16; in N Amm hydroxide 256 nm, log $E_m$ 4.24 (Refs 8 & 9)

**Barium.** Pptd by the addn of Ba chloride to w-sol salts of MEDNA (Refs 2 & 3); it has the least expl efect in lead plate test when primed with MF (Ref 7)

**Cadmium.** It is ranked between the Cu and Ba salts in expl efect in lead plate test when primed with MF (Ref 7)

**Calcium.** It is pptd when Ca chloride soln is added to a w soln of the Na salt (Ref 3)

**Cesium.** Impact sensy on PA app 4 inches (MF 2 inches) (Ref 11)

**Copper.** Impact sensy on PA app 4 inches (Ref 9); it is ranked between Fe and Cd salts in expl efect when primed with MF (Ref 7)

**Monohydroxylamine.** The UV spectrum was studied by R.N. Jones of the Univ of Toronto, cited in Ref 8

**Iron** (valence not stated). It is ranked between the K and Cu salts in expl efect in lead plate test when primed with MF (Ref 7)

**Lead.** It is pptd when a soln of a lead salt is added to a w soln of the Na salt (Ref 3); ign point 250°; impact sensy on BM app, 65cm (50% explns)(Ref 12); PA app 7 inches (MF 2 inches) (Ref 11). It is useful as a detonator when mixed with Pb Picrate, Pb Styphnate, or similar salts (Ref 5)

**Mercury.** Ign point 195° (Ref 12)

**Potassium.** Prepn from the Na salt: to a soln of 30g of the Na salt (see below) in 150ml of w is added a soln of 56.1g of Ag nitrate in 150ml of w, the curdy Ag salt filtered on a Büchner funnel, washed on the filter with 450ml of w, the damp salt suspended in 200ml of w, and the suspension added slowly with stirring to 33.2g of K iodide in 150ml of w. The mixt is stirred for 3 hours, allowed to stand 16 hours, the pptd Ag iodide filtered off, and the w removed in vacuum to give 18.8g (85%) of a gray solid. This is dissolved in 50ml of hot w, clarified with Celite, and cooled to 0°. A small amt of solid is filtered off, and the w evap as above to give 13.5g (61%) of an almost white soln which analyzed as CH$_3$N$_4$O$_4$K$_2$·½H$_2$O (Ref 10). It is ranked between Na and Fe salts in expl efect in lead plate test when primed with MF (Ref 7); impact sensy on PA app, 3 inches (MF 2 inches) (Ref 11)

**Rubidium.** Impact sensy on PA app, 3 inches (Ref 11)

**Silver.** Prepn by addn of Ag nitrate soln to a soln of the Na salt (see above) (Refs 3 & 10); ign point 181° (Ref 12). When treated with alkyl iodides it gives alkyl esters. From the reaction with Me iodide a colorless and a yellow dimethyl ester were isolated (Ref 3). The UV spectra of the colorless (called α) and the yellow (called β) esters are given in Ref 9; it is concluded that the color of the β ester is due to a nitroso group, hence its structure is probably (CH$_3$ON)$_2$CH$_2$}

**NO**

**Sodium.** Prepn by Traube proc: Na metal (13.8g) is dissolved in 300ml of anhyd et alc, the soln cooled to 6° under N, 34.8g of acet added slowly with vigorous stirring as nitric oxide is passed in at 320ml/min for 140min, and the fine yellow solid collected on a Büchner funnel. This damp solid is dissolved in 130ml of w, made just acid with glacial acetic acid, and the soln heated on a steam bath until gassing ceases. The mixt is poured into 400ml of ice cold et alc to give 25.3g (39%) of a brown solid which is recrystd twice from et alc:w 2:1 to give a white solid which decomposes without melting at 225–60° and analyzes as a dihydrate
(Ref 10). Its impact sensy on BM app is 75cm (Ref 12), and is ranked between the Sn and K salts in expl effect in lead plate test when primed with MF (Ref 7)

**Thallium.** Ignition point 208° (Ref 12); has greatest expl effect in lead plate test when primed with MF (Ref 7). It is a useful detonator at d 1.1—1.2g/cc, but usefulness decreases at higher d (Ref 7)

**Tin.** Is ranked between Tl and Na salts in expl effect in lead plate test when primed with MF (Ref 7)

*Written by: C. H. McDonnell*


**MeEDNA** (N-Methylthlenenedinitramine or N-MethyldENA). Structure O₂NNHCH₂CH₂NCH₃, C₃H₅N₄O₄.

\[ \text{NO}_2 \]

**me** 164.13, N 34.14%; OB to CO₂ –58.5%; crysts; mp 120.5—22° (Refs 1, 2 & 5). The compd was first prepd in 1888 by the action of Me iodide in alc K hydroxide on EDNA (Ref 2), but no further work was done until WWII when the expl props of MeEDNA were examined at ERL (Ref 3). Other prepn are by the methylation of EDNA with dimethyl sulfate in aq K hydroxide (Ref 7); and by the action of nitric acid in acet anhyd on the compd O₂NNHCH₂CH₂NCH₃ (Ref 5)

\[ \text{NH}_2 \text{NO}_2 \]

**Best Laboratory Preparation.** A soln of 82.4g of 3-nitrazabutylamine in 100ml of dry benz was placed in a 500ml 3-necked flask fitted with a stirrer, dropping funnel, and thermometer. The soln was cooled in an ice bath, 75ml of acet anhyd added dropwise, the pptd white solid collected, and dried to give 71g (64% yield) of N-acetyl-N₁-methyl-N₁-nitroethylene-diamine, mp 79—80°. This compd (20g) was added in small portions to a mixt of 100ml of 100% nitric acid and 100ml of acet anhyd cooled to —10 to —5°. The mixt was stirred for 45 mins, poured onto crushed ice, the solid filtered, washed with w, and dried to give 9.5g (37.1% yield) of N-acetyl-N₁-methyl-EDNA, mp 55—56°. To 7.6g of this compd was added 25ml of 14% aq ammonia, whereupon it dissolved with evolution of heat. The soln was cooled, acidified with dil HCL, the pptd solid filtered, washed with cold w, and dried to give 5.1g (84.3% yield) of MeEDNA, mp 118—21°, recrystd from ethylene dichloride, mp 121—22° (Ref 6)

**Properties.** Slightly sol in w, sol in eth & chloroform (Ref 2). UV spectrum in et alc, \[ \lambda_{2375} \mu \text{m}, E_{\text{max}} 12950; \] K salt in 0.2N hydrochloric acid, \[ \lambda_{2360} \mu \text{m}, E_{\text{max}} 12200\) (Ref 4)

**Explosion Temperature.** Does not expl to 360° (Ref 3)

**Hygroscopicity at 25°.** No wt gain at 90% RH, 3.77% at 100% RH (Ref 3)

**Impact Sensitivity.** BM app, above 90cm (Ref 3)

**International Heat Test at 75°.** Loses 10.7% by wt (Ref 3)

**Power by Ballistic Mortar.** 120% of TNT (Ref 3)

**Thermal Stability at 135°.** Not acid after 300 min (Ref 3)

**Vacuum Stability at 120°.** Over 12ml evolved in 26—48 hours (Ref 3)

*Written by: C. H. McDonnell*


Meerscheidt-Hüllessem Stability Tests. J. von Meerscheidt-Hüllessem published a series of papers from 1926 to 1939 describing various stability tests for propylnts and NC. Some of the tests were modifications of existing methods and others were original. Ref 1 describes a weight loss method in which 10g samples were heated in test tubes in a thermostatic bath at 115° with weights taken every 8 hrs. In Ref 2, 2.5g samples were heated at 120° or 135° until litmus paper, suspended inside the app, turned pink. Ref 3 describes a new thermostatic bath for detg stability on heating at 75°. Ref 4 covers the detn of the stability of propylnts from the vol of gases of decomr at const press and temp. Modifications made in the Berrmann-Junk-Mayrhofer test (see Vol 2, B102-R) are given in Refs 5, 6 & 7, while small changes in the method of Ref 4 are described in Ref 8. Ref 9 contains a method for detg the chemical stability of exps and propylnts at 120° by collecting evolved gases in a burette and then analyzing them by titration or by detg the acidity of a w soln


Megadina (Megadyne). Belg expl contg Amm perchlorate 78, paraffin wax 16 and Al powd 6%
Refs: 1) CondChemDict (1942), 290 2) A. Pérez Ara (1945), 247

Meganit. A dynamite contg NG 60, nitrated wood pulp 10, nitrated ivory nut meal 10 & Na nitrate 20%
Refs: 1) Naoum, NG (1928), 284 2) PATR 2510 (1958), Ger 112-L

Meganites. Dynamites manuf in Hungary. One of the compns is as given above under "Meganit". Two other compns are: (1) NG 38.0, Nitroglycerine 6.0, Na nitrate 37.5, nitrated ivory nut meal 6.0, sawdust 12.0 and Na carbonate 0.5%, and (2) NG 7.00, Nitroglycerine 9.00, Na nitrate 56.25, nitrated ivory nut meal 9.00, rye flour 18.00 and Na carbonate 0.75%
Ref: Daniel (1902), 434

MELAMINE AND DERIVATIVES

Melamine (2,4,6-Triamino-s-triazine, Cyanurotriamide, Cyanuramide). C₃H₆N₆, mw 126.13, N 66.64%, OB to CO₂ -114.2%; colorl monocrystals, mp 354° (decomp), bp subl, RI 1.8772

at 20°, d 1.573g/cc. Si sol in cold w, sol in hot w (0.32g/100g at 20°, 0.60g at 35°, 1.05g at 50°, 2.4g at 75° and 5.14g at 100°), si sol in alc, insol in eth & acet. Can be prep by the fusion of dicyandiamide with an acid salt of guanidine, and subsequent purification of the prod (Ref 6), or polymerization of dicyandiamide in an electric arc with N and NH₃ (Ref 9). Melamine has been used as a flash reducing agent in propylnts (Ref 10). It is nonhyg, of low volatly, highly resistant to hydrolysis up to 60°, and is practically neutral inaq solns (pH 7.7). Tests conducted at PicArsn indicated satisfactory impact sensitivity (40 inches with 2kg wt), and no sand crushed in the Sand Test bomb

Melamine Dinitrate (N,N'-dinitroammeline), C₃H₃N₂O₅, mw 217.13, N 45.17%, OB to CO₂ -18.4%, mp 228° (decomp). It was prep and

\[
\text{NHNO}_2
\]
tested during WWII in Ger & the USA and was found to be an expl less sensitive and less powerful than TNT. Cason (Ref 5) directly nitrated melamine with nitric acid in the presence of Ac₂O at 5°C to obtain it as a prod, and Atkinson and Whitmore (Ref 8) elucidated its structure

**Trinitromelamine.** C₃H₅N₅O₆, mw 261.05, N 48.28%, OB to CO₂ −9.2%.

![Trinitromelamine structure](image)

The existence of this compd is uncertain. Ref 7 states that the work by Cason (Ref 5) left the whole problem of synthesizing trinitromelamine in a confusing state. It was therefore important to detn whether this compd could be prep’d and whether its performance would show this particular triazine ring to have phosporific value. Atkinson & Whitmore (Ref 8) showed that the chances of a successful prep of trinitromelamine was close to being impossible because of extreme hydrolytic susceptibility. They found the closest approach to the desired compd was N,N'-dinitromellamine (Melamine Dinitrate), which has reasonable stability. They further stated that the Qₐ value for this compd gave no encouragement to the thought that sym-triazine is a useful phosporific group

**Melamine Picrate.** C₆H₆N₇C₆H₃O₄N₃; mw 355.27, N 35.49%, OB to CO₂ −69.8%; light yellow powd.; mp 316−17°C; nearly insol in w. May deflagrate when heated rapidly (Refs 1, 2, 3 & 4)


**Melamina.** Ital dynamite invented in 1873 consisting of NG absorbed in a mixt of powd charcoal and siliceous earth

**Ref:** Davis (1943), 198

**Melanite.** Fr expl contg NG 83−87, NC 17−13%

**Ref:** Daniel (1902), 434

**Mélénite.** Gelatinized expl used in Belg

**Ref:** Daniel (1902), 434

**Melinite.** Fr expl used in shells. The original "Melinite" was composed of 70ps PA mixed with 30ps NC, disd in acet or eth-alc (Ref 1). Later Melinities were either 100% PA or PA to which some quantities of other aromatic nitrocompds were added in order to reduce the mp of PA (120−122°C), thus facilitating casting operations (see under Picric Acid)

**Refs:** 1) Daniel (1902), 434−6 2) CondChemDict (1942), 290 3) Davis (1943), 166

**Meland Powder.** Prep'd in Engl in 1865 by soaking paper sequentially in boiling acq solns of K chlorate, K nitrate and K ferrocyanide. This was followed by rolling the paper thru powd charcoal and then treating it with K chromate and starch. The paper was then rolled to form cartridges, dried at 100°C, and waterproofed with a soln of nitrostarch in acet ac

**Ref:** Daniel (1902), 436

**Melling Powder.** Brit permissible expl contg Amm nitrate 51−55, Amm oxalate 18−20, Na nitrate 11−13, TNT 5−7, NG 4−6 and wood flour 3−5%

**Ref:** CondChemDict (1943), 290

**Melsens Powder.** One of the earlier "progressive smokeless powds". Its grains were ball shaped with outer layers burning more slowly than inner layers

**Ref:** Daniel (1902), 653
Melting Point (mp). The melting point or freezing point of a pure sub is the temp at which its cristal is in equil with the liq phase at atm press. It is usually called the mp when the equil temp is approached by heating the solid. Ordinarilly, mp refers to temps above 0°C, the mp of ice (Ref 1). As the mp of a solid sub which does not subl or decom is one of the best criteria of its purity or identity, the detn of mp is of considerable importance. The presence of even small amounts of impurity may alter the mp considerably, usually lowering it. The mp of typical expl and propnt materials are given below (Ref 2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Formulation or Chemical Name</th>
<th>MP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baratol</td>
<td>24/76 TNT/Ba nitrate</td>
<td>79–80</td>
</tr>
<tr>
<td>Boracit</td>
<td>40/60 TNT/Boric Acid</td>
<td>79–80</td>
</tr>
<tr>
<td>BTF</td>
<td>Benzotriuroxan</td>
<td>198–200</td>
</tr>
<tr>
<td>Comp B, Grade A</td>
<td>36/63/1 TNT/RDX/Wax</td>
<td>~80</td>
</tr>
<tr>
<td>Comp B-3</td>
<td>40/60 TNT/RDX</td>
<td>79–80</td>
</tr>
<tr>
<td>Cycloktol 75/25</td>
<td>75/25 RDX/TNT</td>
<td>79–80</td>
</tr>
<tr>
<td>DATB</td>
<td>1,3-Diamino-2,4,6-trinitrobenzene</td>
<td>286</td>
</tr>
<tr>
<td>DiPAM</td>
<td>Dipicrylamine</td>
<td>304</td>
</tr>
<tr>
<td>HMX</td>
<td>Cyclotetramethylene tetranitramine</td>
<td>285–287</td>
</tr>
<tr>
<td>HNAB</td>
<td>2,2',4,4',6,6'-Hexanitroazobenzene</td>
<td>215–216</td>
</tr>
<tr>
<td>NC (12.0% N)</td>
<td>Nitrocellulose, lacquer grade</td>
<td>135 dec</td>
</tr>
<tr>
<td>NC (13.35% N, min)</td>
<td>Nitrocellulose, gun cotton</td>
<td>135 dec</td>
</tr>
<tr>
<td>NG</td>
<td>Nitroglycerin</td>
<td>13.2</td>
</tr>
<tr>
<td>NGu</td>
<td>Nitroguanidine</td>
<td>246–247</td>
</tr>
<tr>
<td>Octol</td>
<td>25/75 TNT/HMX</td>
<td>79–80</td>
</tr>
<tr>
<td>PETN</td>
<td>Pentaerythritol Tetranitrate</td>
<td>139–142</td>
</tr>
<tr>
<td>RDX</td>
<td>Cyclotrimethylene trinitramine</td>
<td>204</td>
</tr>
<tr>
<td>Tetryl</td>
<td>2,4,6-Trinitrophenylmethylnitramine</td>
<td>130</td>
</tr>
<tr>
<td>TMN</td>
<td>Tetranitromethane</td>
<td>14.2</td>
</tr>
<tr>
<td>TNT</td>
<td>2,4,6-Trinitrotoluene</td>
<td>80.9</td>
</tr>
</tbody>
</table>

Ref: 1) CondChemDict (1971), 548 2) B.M. Dobratz, "Properties of Chemical Explosives and Explosive Simulants", UCRL-51319, Lawrence Livermore Laboratory, Univ of Calif (Dec 1972), 4-6 to 4-7

Melting Point, Determination. Most methods for the detn of mp are microprocedures, and may be conveniently classified on the basis of the type of app used for the detn: (1) the capillary tube method, (2) the heating bar method, and (3) the microscope heating stage (micro hot stage) method.

The capillary tube method initially involves packing a powdered sample into a glass capillary tube of uniform diameter and length, carefully sealed at one end so that it forms a rounded tube of uniform thickness. The tube is then attached to a standardized thermometer so that the end of the tube reaches the middle of the thermometer reservoir bulb. This assembly is then inserted into a vessel contg a suitable liq which is uniformly heated so that the temp rises at a rate of about 1° per minute. Ref 1 discusses in detail equipment design and thermometer calibration. It should be noted that this technique is the method most widely used by organic chemists for mp detns, and that most of the mp's of organic compds cited in the literature were obtained in this manner.

The heating bar method, utilizing heating bars, blocks or benches was developed primarily to overcome some of the shortcomings of the liq bath app (discoloration and fuming at high temps), and to obtain better temp control so as to provide a more accurate measurement of the melting temp. Three general types exist, (1) a simple type heated by a gas flame, in which the temp is recorded by a thermometer, (2) an electrically heated type, with a thermometer to record the temp, and (3) an electrically heated
type, with a thermocouple and potentiometer for temp measurement (Ref 2)

For more precise work, micro hot stage methods under a microscope are used. For all comds except those which are isotropic or become so on heating, the mp can best be observed by means of a polarizing microscope, since the temp at which color disappears and the space lattice is ruptured is the true mp. Among numerous models of micro-hot stages, the Kohler micro-hot stage has attained widespread use and is commercially available (Refs 3 & 4)


Melville Powders. Expls invented in 1850 consisting of K chlorate, K ferrocyanide and As tribromide
Ref: Daniel (1902), 436

Mendeleyev, Dmitry I. (1834–1907). "Distinguished Rus scientist best known as creator of the Periodic System of the Elements. Inventor of one of the first successful single-base NC propnls using “pyrocolloidion” which was adopted by the Rus Navy in 1895. The same powd, with slightly higher N content, was later introduced in the US Navy
Refs: 1) A. Sapajnokoff, SS 2, 161–64 (1907) 2) W.A. Tilden, JCS 95, 2015–77 (1909) 3) A. Pérez Ara (1945), 449

Mendoça-Corteso Powder. Portuguese propnl similar to Cordite (see Vol 3, C531-R)
Ref: Daniel (1902), 437

MeNENA. Designation for N-(β-nitroxyethyl) methylnitramine, described under N-(β-hydroxyethyl) methylnitramine in Vol 7, H241-R

Me₂NENA. Designation for N-(2-nitroxypropyl) methylnitramine, described under N-methyl-N-(2-nitroxypropyl) nitramine in this Vol

5-Mercaptotetrazole (5-Tetrazolethiol). CH₂N₄S, mw 102.13, N 54.93%; needles from alc, mp 205° (dec at about 206–210°);

\[
\text{HSC} \quad \text{NH} \quad \text{HSC} \quad \text{N} \\
\text{HN} \quad \text{N} \quad \text{N} \quad \text{HN} \quad \text{N} \quad \text{N}
\]
sol in eth, meth, et acet and w, nearly insol in bz and chlf. Can be prep'd by heating 5-methyl-mercaptopentazole with concd hydric acid in the presence of AcOH. In a purer state, it may be prep'd by acidifying the Na salt of mercaptotetrazole with sulfuric acid (see below). Forms salts, some of which are sl expl (see below)

Sodium Mercaptotetrazole. NaCHN₄S, mw 124.11, N 45.15%; colorl needles. Can be prep'd by adding to the prod of the reaction between methylmercaptoetrazole and acy hydracid a sufficient amt of soda soln to make the reaction sl alkaline (Ref 2). The resulting crystal compd cont 1.5 mols of w. It is sol in w and alc, less sol in abs alc, insol in eth. May be obtd in a very pure state by dissolving in w andppt with eth. Such crystall would give pure 5-mercaptopentazole on acidifcation with sulfuric acid
Refs: 1) Bell 26, 409 2) M. Freund & T. Paradies, Ber 34, 3117–18 (1901)

Mercerized Cellulose (Mercerized Cotton). Mercerization is a process of treating cotton with 25% Na hydrxide which causes it to shrink and become heavier, stronger, denser, and acquire a milky luster; it will not shrink and is more easily dyed. It is more active and easier to nitrate than the original cellulose, but the resulting prod is not very stable
Refs: 1) Hack’s (1944), 523 2) Dorée (1947), 84

Mercuric-Ammonium Salts. Several expl compds of general formu Hg₂NX, where X is either NO₂, ClO₃, ClO₄, IO₃, CrO₄, MnO₄ or BO₃, were prep'd by double decomp of Hg₂NiNO₃ with salts of NH₄, Na and K. Trinitrobenzoate, picare, acetylde and azide compds of Hg₂N are very expl. Compds in which X=I, CNO, SCN or sthyphate do not deton but defgr or burn away
MERCURY AND ITS SALTS

Mercurit. Ger blasting expl contg K chlorate 88 and a high bp neutral tar oil 12%. In Mercurit II, up to 20% of the chlorate was replaced by perchlorate. Ref: Marshall, Dict (1920), 60

Mercury (Quicksilver, Hydrargyrum), Hg, at wt 200.61, silvery liq, mp –38.87°, bp 356.9°, d 13.546g/cc at 20°. Insol in w, HCl, alc and eth; sol in nitric acid. Sometimes found native; poisonous. Can be prepd by heating the ore cinnabar (HgS) either in air or with lime. Forms numerous salts, some of which are very expl, eg, Hg fulminate, Hg azide, etc. The presence of Hg in expls, even in minute quants, is undesirable because it affects the result of thermal stability tests. Marshall (Ref 1) describes various tests used in Engl and Ger for its detection in different expls and proplnts. Refs: 1) Marshall 2, 708–12 (1917) 2) Mellor 4, 695, 768 (1927) 3) CondChemDict (1950), 429 4) Sax (1968), 902-R

Mercury Azide. See under Azides (Mercuric and Mercurous)

Mercury (Mercurous) Chlorate. See under Chlorates

Mercury (Mercuric) Chlorite. See under Chlorites

Mercury Fulminate. See under Fulminates, Vol 6, F217-L

Mercury, Fulminating. See Vol 6, F232-L

Mercury Nitride. See under Fulminating Mercury

Mercury as Masking Agent. Mercuric salts such as HgCl₂ were frequently added to wet NC to prevent mold formation. Their presence also allowed defective NC to pass the K iodide-Starch heat (thermal stability Abel's Test) test (Ref 2). According to F.L. Nathan (Ref 3) the Hg of HgCl₂ acted on the iodine liberated in the test paper by nitrous acid fumes, forming a colorless substance and thus masking the color reaction on the paper. Non-vol Hg salts did not affect the test. The usual tests for Hg could not be used because of the difficulty in extrg the salts from org material. A variety of test procedures were proposed to detect Hg salts in micro quantities in NC and expls (Refs 1, 4, 5 & 6)


Mercury (Mercuric) Oxycyanide. HgO.Hg(CN)₂, mw 469.26, N 5.97%; wh cryst powd, mp (expls on heating), d 4.437g/cc at 19°, poisonous; moderately sol in w, nearly insol in alc, eth and bz. Used as an antiseptic. Can be prepd by heating 10ps Hg cyanide with 10ps Hg oxide in 100ps w, or by other methods (Ref 4). Its expl props were investigated by Kast and Haid (Ref 3), and it was found to be a weak expl. Some of its expl props are as follows, compared with BrFdr as detd by the same investigators, shown in brackets: Trauzl block expansion, 10cc; Sp Energy, 2090kg/l (2810); Qc, 138cal/g (665); Vol of gases of expl, 190l/kg (280); Temp of Expl, 2620° (2380°); Impact Sensitivity with 2kg wt, 60cm; Friction Sensitivity, snaps; behavior in open flame, weak deflagration. Note: An expl took place in Philadelphia in 1916 as mercuric oxycyanide was being transferred from a factory container to storage bottles. The cause was not known (Ref 2)

**Mercury Phenyl Nitrate** (Hydroxymercuribenzenec nitrate). C₆H₅HgON₂, mw 339.72, N 4.12%; plates from alc; mp 188–89° (decompn); very sol in hot w, sol in bz and hot alc. Can be prepd by mixing a cold chif soln of NO₂ with Hg DPhA, or by other methods. It is mildly expl

*Refs:* 1) Beil 16, 953 & (563) 2) E. Bamberger, Ber 30, 511 (1897)

**Mercury Perchlorates.** Are not expl

**Mercury Picrate.** See under Picrates

**Mercury (Mercuric) Sulfocyanate** (Mercuric thio cyanate, Mercureic rhodamide). Hg(SCN)₂, mw 316.77, white powd; mp (decompn), poisonous; sl sol in w (0.07g/100g at 25°), sol in alc and in NH₃ & NH₄ salts. Can be prepd by pptn of Hg nitrate with Amm sulfocyanate and subsequent soln in a large quant of hot w, followed by crystn. Used in prepn of “Pharaoh’s Serpent” and other fireworks (Ref 4)


**Mercury Methazonate.** See under Methazonic Acid in this Vol

**Mérimo.** Pat in 1882 in Fr, a mixt designed for coating grains of hygroscopic ingredients of expl mixts, such as nitrates or chlorates, to render them waterproof. It contd the following: K chlorate 73, NG 10, sulfur 7, caoutchouc or hard pitch 3, resin or soft pitch 1 & anthracite coal 6%  

*Ref:* Daniel (1902), 437

**Mesabi Blasting Agents.** A series of metallized expls originated by Dr M.A. Cook at the Univ of Utah, and manufd since 1961 by Mesabi Blasting Agents, Inc. These expls consist of slurries of finely divided Al-AN, Al-AN-TNT and TNT-AN, and present advantages over AN-fuel oil mixts, conventionally used in mining operations

*Ref:* Anon, C&EN 42, 29 (27 April 1964)

**Mesa Type Propellants.** An increase in the press at which a propint is burned increases the rate of heat transfer from the flame to the propint by increasing the density of the gas phase and thereby decreasing the thickness of the region thru which the heat must be transferred, thus increasing the burning rate. The relationship is most commonly expressed by the equation R=bPⁿ, where R is burning rate and P is press, which is known as the de Saint Robert or exponential burning rate equation. If a log P vs log R plot is made for many proplnts, a family of curves is obtained from which the values of b and n can be evaluated (Fig 1). Some proplnts will not follow this straight-line log relationship and may demonstrate regions of nonconstant, reduced, or negative n. When n is markedly reduced, as shown in Fig 2, the propint is known as a plateau (from the shape of the curves) propint. When n becomes negative for a portion of the press range, as shown in Fig 3, the propint is called a mesa type propint

![Rate-Pressure Relationship of Propellants for Which R = bPⁿ](image)

Fig 1 Rate-Pressure Relationship of Propellants for Which R = bPⁿ


MESITYLENE AND DERIVATIVES

Mesitylene (2,3,5-Trimethylbenzene).
\[ \text{C}_6\text{H}_3(\text{CH}_3)_3 \text{, mp 120.20, color liq, fp } -44.7^\circ \text{, bp 164.7}^\circ \text{ at 760mm, 48.7}^\circ \text{ at 40mm, d 0.8652 g/cc at 20/4}^\circ, \RI{1.4994} \text{ at 20}^\circ. \text{ Insol in w, misc with alc, eth, acet, benz } \& \text{CCI}_4. \text{ Can be prepd by heating benz with 3 moles of formic acid methyl ester } \& 5 \text{ moles of AlCl}_3 \text{ at } 80–100^\circ \text{ (Ref 2).}

During oxidn of mesitylene with nitric acid in an autoclave at 115\(^\circ\) to give 3,5-dimethylbenzoic acid, a violent expln occurred. The reaction was attributed to local overheating, formation of a trinitro compd, 1,3,5-tri (nitromethyl) benzene, and to violent decompn of the latter. Smaller scale prepns with better temp control were uneventful (Ref 3).


2-Azido-4-nitro-mesitylene (2-Azido-4-nitro-1,3,5-trimethyl benzene). \[ \text{C}_6\text{H}_4\text{O}_3\text{N}_4 \text{; mw 206.23, N 27.17\%, OB to CO}_2 = 155.17\%, \text{Needles-H}_2\text{O} \text{ (from aq eth), anhyd crystals (from abs eth), mp 23\(^\circ\). Can be prepd by adding Na azide to a soln of 4-nitro-mesitylene-diazonium chloride (2) (Ref 2). Expls on fast heating in all org solvs. Loses 2/3 of its N content in concd sulfuric acid.}

2,4-Diazido-mesitylene (2,4-Diazido-1,3,5-trimethyl benzene). C₆H₅N₄, mw 198.21, N 42.41%. Yellow oil, pleasant fruity odor, turns brown in light. Can be prepd by the diazotization of 2,4-diamino-mesitylene by heating with Na azide in the presence of Na nitrite in alc. HCl (Ref 2). Decomposes on heating; emits white fumes in sulfuric acid.


2,4-Diazido-6-nitro-mesitylene (2,4-Diazido-6-nitro-1,3,5-trimethyl benzene). C₆H₅O₂N₄, mw 247.25, N 39.66%, OB to CO₂ −132.66%, clear yellow needles from petr eth; mp 50°C. Can be prepd by treating 2,4-diamino-6-nitro-mesitylene with Na nitrite under cold conditions (Ref 2). Decomposes on heating; emits N₂ in concd sulfuric acid.


2,4,6-Triazido-mesitylene (2,4,6-Triazido-1,3,5-trimethyl benzene). C₆H₅N₃, mw 243.27, N 51.83%, needles from pet eth; mp 50°C. Can be prepd by treating 2,4,6-triamino mesitylene in HCl with 6 moles of Na nitrite in dil HCl in the presence of NaN₃ at −5°C (Ref 2). Turns brown in light. Decomposes in concd sulfuric acid with N₂ evolution.


2-Nitro-mesitylene (2-Nitro-1,3,5-trimethyl benzene). C₆H₅NO₂, mw 165.21, N 8.48%, OB to CO₂ −208.22%, rhm crst (from alc); mp 44°C, bp 255°C at 760mm, d 1.51g/cc; v sol in hot alc. Can be prepd by nitration of mesitylene with nitric acid (Ref 2).

Mesityl Oxide (4-Methyl-3-penten-2-one).
(CH$_3$)$_2$C:CHCOCH$_3$, mw 98.15; OB to CO$_2$ -260.83%, mp -52.85$^\circ$, oily, colorless with characteristic honey-like odor; bp 129.76$^\circ$ at 760mm, 41$^\circ$ at 20mm, d 0.865g/cc at 20/4$^\circ$,
RI 1.4440 at 20$^\circ$, vap press 8.7mm at 20$^\circ$; sol in w (3p at 20$^\circ$); sol in benz, miscible with alcohols, ketones and phenols can be violent.
Acetaldehyde oxidizes readily in air to unstable peroxides that may explode spontaneously. Its combination with bromine, chlorine, fluorine or iodine can be violent (Ref 5).

Mesityloxideperoxide (Mesityloxidesuperoxyd in Ger). C$_5$H$_4$O$_7$ (Ref 2), C$_6$H$_4$O$_6$ (Ref 3).
Granular crystals from eth-alc. Insol in w, sol in eth, acet, benz & eth-alc. Prepd by allowing mesityl oxide to remain in H$_2$O$_2$ for several hours. Defflagrates on impact
Refs: 1) Beil 1, 738 & (384) 2) R. Wollfenstein, Ber 28, 2269 (1895) 3) J. Pastureau, Bull Fr [4], 25, 595 (1919)

Metaldehyde (Polymerized acetaldehyde),
(CH$_3$CHO)$_n$; mw 176.21, OB to CO$_2$ -181.60%, colorless cryst, mp 246$^\circ$, subl 112-115$^\circ$, flash p 97$^\circ$; sol in benz & chlf, sol in alc & eth, insol in w. For prep of acetaldehyde & metaldehyde see Vol 1, A14. Used as a substitute for gum lacquer in illuminating comps developed after WWI. It burned without leaving any slag and reduced compn sensitivity to impact (Ref 1).
Urbanski & Wozniak (Ref 2) prep'd comps contg metaldehyde 8-11, Ba chloride 80 & lactose 4-9%, and reported deeply saturated green flames on burning. In a compn contg metaldehyde 8, milk sugar 6, K chloride 60 & Sr oxalate 26%, poor propagative burning and a weak red color were obtained.
Metaldehyde is flammable and a dangerous fire risk. It is highly toxic and a strong irritant to skin and mucous membranes (Refs 3 & 4). Its condensation reaction with acid anhydrides,

Metals, Compatibility of Common Explosives With. The following table, compiled from Refs 1, 2, 3 & 6, details the compatibility of dry expls (0.2% moisture max) with metals commonly used in military hardware. For all of the listed metals, except phosphate coated steel, intimate contact was maintained with the various expls at ambient temp for a two year period (Ref 2). Phosphate coated steel was exposed for six months at 71$^\circ$ (Ref 3).
Exposure of moist expls (0.5% moisture) with common metals at 50$^\circ$ for two years (two months at 71$^\circ$ and 100% relative humidity for phosphate coated steel) resulted in from very slight to very heavy corrosion for practically all of the metals shown in the above table.
Stainless steel was unaffected by any expl, acid proof black painted steel was not affected by 75/25 Tetrytol and 50/50 Pentolite, and Mg-Al alloy (J1) was unaffected by BkPdr. Phosphate coated steel exhibited considerable corrosion with BkPdr, but was unaffected by TNT, RDX, Comp B, Tetrytol or 50/50 Pentolite (Ref 3).
An important class of expl materials contains metallic fuels and inorganic oxidants. Examples are Tritonal (TNT/Al, 80/20), Amatols (TNT/AN, 28/80 & 80/20), and Minol-2 (TNT/AN/Al, 40/40/20). Oxidants other than nitrates, such as chlorates and perchlorates, may be employed. Water solns containing these cations are highly corrosive to metals. Alkaline metal salts, for example, in the presence of moisture, will pit Al quickly (Ref 6).
In delay compns, such corrosion problems have resulted in the widespread use of chromates, which, in addition to being insoluble in w, tend to inhibit corrosion (Ref 6).
Of particular interest is the reaction of ni-
<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Titanium</td>
<td>N</td>
<td>A</td>
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<tr>
<td>18-8 Stainless Steel</td>
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<td>N</td>
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<tr>
<td>Bronze</td>
<td>N</td>
<td>DN</td>
</tr>
<tr>
<td>Brass</td>
<td>N</td>
<td>C</td>
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<tr>
<td>Monel</td>
<td>N</td>
<td>DN</td>
</tr>
<tr>
<td>Magnesium Alumimun</td>
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<td>N</td>
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<tr>
<td>Phosphorus Coated Steel</td>
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<tr>
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<tr>
<td>Copper Plated Steel</td>
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<tr>
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<td>C</td>
</tr>
<tr>
<td>Magnesium</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

A: Excellent, B: Satisfactory, C: Acceptable, D: Poor, N: Neutral

Table 1: Compatibility of Common Explosives and Metals

Lead Block, Lead Composition

Aid: Powder, Statics, B: Petrol, HDX, Petrol, TNT, Ammonium Nitrate, Tetryl, Emulsion Petrol

50/50 75/25 60/40 50/50
trates with Cu in the presence of moisture. Phillips, at PicArsn, conducted storage tests of Cu foil in contact with AN, 80/20 and 50/50 Amatol solutions containing various percentages of w in both open and closed containers at 50°. In the closed containers, a sensitive, purple tetramino cupric nitrate formed very readily in the presence of AN, less readily with 80/20 Amatol, and to little or no extent with 50/50 Amatol. In open containers there was no formation of the purple salt. In all cases except those in which the minimum amount of moisture was present, there was corrosion of the Cu strips with the formation of blue and green basic nitrates, and it was found that at ambient temps, these basic nitrates would react with Cu to form the sensitive purple salt. It was concluded that no Cu or Cu alloys could be used in ammo which could contact Amatol fillers (Ref 1).

The reaction of Lead Azide (LA) with Cu (see Table) deserves special comment. Although this reaction is relatively slow, even in the presence of w, some forms of Cu Azide are so sensitive that they create a serious hazard even in minute quantities, particularly when in contact with LA. For this reason, Al and stainless steel containers are now used exclusively. PicArsn requires that all new fuze designs contain no Cu or Cu alloys, with the possible exception of the electrical system. Even here, the Cu must be coated for protection against the formation of hydrazoic acid. Another prohibition involves the use of Pb thiocyanate in contact with Al (Refs 4, 5 & 6)

Written by: H. L. HERMAN


Metalline Nitroleum (Nitroglycerin-metal). Dynamite in which powdered red lead (Pb3O4) is used as an absorbsent. Plaster of Paris may be added to the mixt.
Ref: Daniel (1902), 437

Metals, Explosive Working of. See under Explosive Fabrication of Metals in Vol 6, E415-R to E418-R

Meteor Dynamite. A blasting expln manufd in the 19th century by the Oliver Powder Co of Wilkes Barre, Pa, USA. This company also manufd “Oliver’s Flameless Dynamite”
Ref: Daniel (1902), 438 & 590

METHANE AND DERIVATIVES

Methane. (Marsh Gas, Fire Damp), Methan, Sumpgas, or Grubengas (Ger); Méthane or Grisou (Fr); Metan (Russ); CH4, mw 16.04; a colorl, odorless, and tasteless gas; mp -182.5°, bp -161.5°, crit temp -82.1°, crit p 672 psi (Ref 1); CA Registry No 74-82-8
Occurrence. It is the chief constituent of natural gas, which is from 60–98% methane. It occurs to some extent in all coal mines where mixts with air are called by the miners “fire damp” as it is the cause of almost all coal mine fires and explns (Ref 3). It also occurs in the gases evolved when organic matter decomposes anaerobically as in the bottoms of swamps and marshes, hence the name “marsh gas”
Preparation. It can be recovered from the gases produced by the destructive distn of coal (coal gas) or from the prepn of coke (coke oven gas). It can also be prepd by the catalytic reforming of other low-boiling hydrocarbons (ethane to butane) (Ref 3)
Flammability. It is very flammable and forms expl mixts with air; the expl limits are: lower 5.3%, upper 14.0% by vol (Ref 1)
Heat of Combustion. 1009 BTU/cu ft (Ref 3)
Solubility. In w 5.66ccl/100ml at 0°, 9cc/100ml at 20°; in alc 45.1cc/100ml at 20°; in eth 104cc/100ml at 10°; sl sol in oleum (Ref 1)
Specific Heat. 2.48 cal/g betw 10 and 200° & 1 atm p (Ref 2)
Azidomethane (Methyl Azide). (called Azidomethan or Methylazid in Ger): CH₃N₃; mw 57.06, N 73.65%; a colorless, mobile, ethereal liq with an unpleasant odor similar to hydrazoic acid (Ref 2); bp 20-1°C; d₄ 0.869g/cc (Ref 2); CA Registry No 624-90-8

Preparation. It was first prep by warming a strongly alk soln of Na azide with Me sulfite (Refs 2 & 20), and this is the only practical prep. It has also been prep by the reactn of diazomethane with hydrazoic acid (Ref 6)

Chemical Reactions. Upon treatment with anhyd chloride and MeMg iodide in aq ammonia, it gives dimethyltriazene (CH₃N₂H-NHCH₃) (Ref 2). A mixt of Me azide with H reacts in the cold with triphenylphosphine or triethylphosphine to form the phosphine Me imide (R₃P:Me) (Ref 3). It can be hydrogenated over Pd/C to Me amine (Ref 5). Me azide, like other azides, will condense with acetylenes to form 1,2,3-triazoles (Ref 10). It was condensed with either argon or carbon dioxide at 4.2°C and 50% K respectively, and the solid photo-lyzed with a Hg vapor lamp. IR analysis showed the formation of methyleneimine (CH₂:NH) which is further photolyzed to HNC (the unstable parent of isocyanides) (Ref 17). Treatment of Me azide with toluene in the presence of anhyd Al chloride gave a mixt of N-methyltoluidines (Ref 18). Photolysis of Me azide in inert solvs at -80°C gave N and hexamethylenetetramine (Ref 19). Me azide was found to detonate in the presence of traces of Hg, but not in its absence; it was proposed that the deton was caused by the formation of traces of Hg azide (Ref 16)

Explosion Temperature. Above 500°C (Ref 2)

Molar Refraction. The molar refraction of the azido group in alkyl azides was estd to be ca 9.4 (Ref 14). For a discussion of molar refraction see Ref 9, p 528

Spectral Data. Infra Red. The band at 2143cm⁻¹ is assigned to the N-N stretching freq (Ref 12); other freqs are assigned in Ref 13

Mass. The appearance potentials and rel abundance of the ions from Me azide are given in Ref 15

Nuclear Magnetic Resonance. The N-14 NMR peaks for Me azide are at 129.5 ± 0.5, 167.5 ± 0.5 and 305 ± 1 ppm (NMe is std). The farthest upfield peak is due to the N attached to C (Ref 21)

Ultra-Violet. In the vapor phase the UV peak is at 3900Å. In eth it is broadened and shifted to ca 3950Å (Ref 7)

Sensitivity. Its sensitivity is greater than indicated in the earlier literature. An explosion occurred when a sample was being sealed in a closed bomb resulting in loss of eyesight (Ref 11)

Thermal Decomposition. The therm decomp at 245°C is 1st order and a white residue is formed (Ref 4). It was restudied at 200-240°C and 0.08 to 46.6cm of Hg. The decomp was found to be homogeneous and 1st order with a const K of 3.02 x 10⁻⁴e⁻¹·₄·₃·₅₀·₀·₉·₅·₀·₂·₁₀·₄·₅·₁ (Ref 8)

Refs. 1) Bell 1, 56, (1), (1), (1)& (3) 2) H.B. Dixon & J. M. Crofts, JCS 105, 2036 (1914) 3) Kirk & Othner 13, (1964), 364

Azomethane. CA Registry No 503-28-6. The following supplements the article in Vol 1, A655-R under Azomethane

Preparation. It has been prep by the oxind of N₁N₂-dimethylhydrazine with K dichromate (Ref 2). The action of Cu(II) sulfate in aq Na acetate contg HCl, Na chloride, or Cu(II) chloride on the same hydrazine gives the Cu(I) chloride complex of azomethane (Refs 3 & 13)
Chemical Reactions. It burns with a luminous flame and is readily exptd (Ref 2). It is reduced with Zn dust and Na hydroxide to dimethyl hydrazine (Ref 2). Action of concd HCl forms methylhydrazine and formaldehyde (Ref 2). Treatment in anhyd eth with Na metal forms a solid adduct which gives dimethylhydrazine on addn of w (Ref 4). For a review of thermal and photochem reactions see Ref 8

Explosive Limits. In mixts with air the crit press at which expl occurs varies inversely with temp betw 350 and 380°F (Ref 6)

Spectra. Infra-Red. In the vapor phase the major peaks are at 3, 4, 6.9, 9 & 10μ (Ref 9)

Nuclear Magnetic Resonance. A single proton peak is at 6.327 (Ref 12)

Ultra-Violet. There is a single absorption peak at 3390Å (Ref 4)

Viscosity. The visc of the gas is 0.754 x 10⁻⁴ ± 1% poise (Ref 7)

Uses. It is a source of free Me radicals (Ref 8). Its addn at a level of 0.1–5.0% was found to improve the octane rating of diesel fuels (Ref 10)

Cuprous Chloride Complex. For prepn see above. It is a red cryst solid, readily decompd into its components at 140–400°C (Refs 4 & 13). X-ray diffraction showed that the azomethane molcs lie betw the infinite folded sheets of the Cu(I) chloride (Ref 11). The complex is used in the prepn of highly pure samples of azomethane (Ref 7)


Azo-Halogen Derivatives of Methane

1,1,1-Trifluoroazomethane, F₃CH:CH₂NCH₃, mw 112.05, N 25.00%; bp 2.6°C; CA Registry No 690-21-1. Prepd by the action of CF₃NO on Me amine in a sealed tube or autoclave


Pentafluoroazomethane, F₅CN:NCHF₂, mw 148.04, N 18.93%; bp –9°C. Prepd by fluoronation of F₅CN:NCH₃ with Co trifluoride or Mn trifluoride

Refs: 1) Beil – not found 2) A.S. Filatov et al, ZhObshchKhim 38, 33 (1968) & CA 69, 18501y (1968)

Hexafluoroazomethane, CF₃N:NCF₃, C₂F₆N₂, mw 166.04, N 18.68%; a gas whose color has been described as colord (Ref 6), greenish (Ref 2), and pale greenish yellow (Ref 5); mp –133°C; bp –31°C; d 1.487g/cc (Refs 1 & 2); CA Registry No 372-63-4

Preparation. A compd C₂F₆N₂ was reported in 1936 among the prods of the action of F on Ag cyanide (Ref 2), but the structure was not proved until 1940, when it was prepd in good yield by the action of I pentafluoride on I cyanide (Ref 4). Since then it has been prepd as the major prod from the action of Ag difluoride on cyanogen chloride (Refs 6 & 10); by the interaction of Cl, Na fluoride, and cyanogen chloride in a sealed tube at 50°C for 1 hour (Refs 9 & 10); and in low yields by the fluorination of ethylene diamine or ethyleneimine (Ref 7)

Chemical Reactions. Its thermal decompn in toluene gives N and hexafluoroethane plus small amts of tetrafluoromethane and tetrafluoroethylene (Ref 8). Photolysis of the gas gives N, hexafluoroethane, and higher boiling prods; higher press favors the formation of the high boiling prods (Ref 5)

Dielectric Coefficient. In the gas phase it is 0.46 x 10⁻¹⁸ (Ref 3)

Explosive Properties. In the gas phase it expl on contact with a flame or an elec spark (Ref 4). This expln gives an extremely high rate of press development, indicating it to be more hazardous than acetylene in press systems (Ref 9)
Heat of Vaporization. At $-31.6^\circ$ it is 5470 cal/mole (Ref 4).

Spectra. Infra-red. In the gas phase the peaks are at 7.16, 7.91, 8.32, 8.80 and 9.10 m$^{-1}$ (Ref 9).

Ultraviolet. In Me chloride an absorption peak is at ca 360 m$^{-1}$ (Ref 9).


1-Chloro-1,1-difluoroazomethane, ClCFCN:NCH$_3$, mw 128.51, N 21.80%; bp 44$^\circ$; at 20$^\circ$, 1.871 g/cc. Prepd by reduction of ClCNF$_2$NO and Me amine.

Refs: 1) Bell — not found 2) S.P. Makarov et al, Dokl Akad Nauk 141, 137 (1961) & CA 56, 11245g (1962)

1-Chloro-1,1,1-trifluoroazomethane, F$_3$CN:NCH$_2$Cl, mw 146.50, N 19.12%; bp 47–48$^\circ$; at 20$^\circ$, 1.4400g/cc, RI at 20$^\circ$, 1.3780. Prepd by action of Cl on F$_3$CN:NCH$_3$.

Refs: 1) Bell — not found 2) A.S. Filatov et al, Zh Obshch Khim 38, 33 (1968) & CA 69, 18501y (1968)

Chloropentafluorooazomethane, CIF$_2$N:NCF$_3$, mw 182.50, N 15.36%; bp 4.5$^\circ$; prep not given in Refs.

Refs: 1) Bell — not found 2) V.A. Ginsberg et al, Dokl Akad Nauk 142, 88 (1962) & CA 57, 642e (1962)

1,1-Dichloro-1,1,1-trifluoroazomethane, Cl$_2$CHN:NCF$_3$, mw 180.95, N 15.48%; bp 80$^\circ$; at 20$^\circ$, 1.4518g/cc, RI at 20$^\circ$, 1.3860. Prepd by the action of Cl on F$_3$CN:NCH$_3$.

Refs: 1) Bell — not found 2) A.S. Filatov et al, Zh Obshch Khim 38, 33 (1968) & CA 69, 18501y (1968)

1,1-Dichlorotetrafluoroazomethane, ClCIF$_2$N:NCF$_2$Cl, mw 198.94, N 14.08%; bp 40.5$^\circ$; at 20$^\circ$, 1.458g/cc, RI at 20$^\circ$, 1.3275. Prepd not given in Refs.

Refs: 1) Bell — not found 2) V.A. Ginsberg et al, Dokl Akad Nauk 142, 88 (1962) & CA 57, 642e (1962)

1,1,1-Trichlorotrifluoroazomethane, Cl$_3$CN:NCF$_3$, mw 215.48, N 13.01%; bp 55$^\circ$ at 920mm; at 20$^\circ$, 1.6147g/cc, RI at 20$^\circ$, 1.4628. Prepd by action of Cl on F$_3$CN:NCH$_3$.

Refs: 1) Bell — not found 2) A.S. Filatov et al, Zh Obshch Khim 38, 33 (1968) & CA 69, 18501y (1968)

1,1,1-Trichlorotrifluoroazomethane, Cl$_2$CFN:NCF$_2$Cl, mw 215.48, N 13.01%; bp 78$^\circ$; at 20$^\circ$, 1.513 g/cc, RI at 20$^\circ$, 1.3275; prep not given in Refs.

Refs: 1) Bell — not found 2) V.A. Ginsberg et al, Dokl Akad Nauk 142, 88 (1962) & CA 57, 642e (1962)

Bromopentafluorooazomethane, BrCIF$_2$N:NCF$_3$, mw 226.95, N 12.35%. Prepd by the reaction of Ag difluoride with Br$_2$CN:CB$_3$.

Refs: 1) Bell — not found 2) R.A. Mitch & P.H. Ogden, JOC 31, 3833 (1966)

All the halogenated azomethanes are yellow gases or liquids which expl on heating.

Refs: 1) V.A. Ginsberg et al, Dokl Akad Nauk 142, 88 (1962) & CA 57, 642e (1962)

Azoxy Derivatives of Methane

Azoxymethane. CA Registry No 25843-45-2. The following supplements the article on Azoxymethane in Vol 1, A470-L. It has been prep'd by the extractive condensation of nitromethane in IN aq H$_2$SO$_4$, with N-methylhydroxylamine as an intermediate, yield 60% (Ref 4).

The proton NMR spectrum shows chem shifts of 6.93 and 5.95$^\tau$ (Ref 1). Photolysis with a Hg arc lamp gives N, nitrous oxide, methane, and ethane (Ref 2). It was found to produce colon and neoplastic tumors in rats after oral administration at 12mg/kg weekly, induction period 235 days (Ref 3).


1,1,1-Trifluorooazomethane. F$_3$CN(O):NCH$_3$, mw 128.06, N 21.88%, OB to CO$_2$ -68.72%; bp -15$^\circ$ at 150mm; N 20$^\circ$, 1.349g/cc. Prepd by the interaction of CF$_3$NO and CH$_3$NOH


Hexafluoroazomethane. F$_3$C(N$_2$O)CF$_3$, mw
182.04, N 15.39%; bp 6.9°, Q_vap 6410
cal/mole (Ref 2); CA Registry No 371-56-2. It
was first prep'd by the reaction of F_3CNO with
activated C in a sealed tube at 150° for 1 hour,
yield 47% (Ref 2). More recent preps are by
the reaction of F_3CNO with guanidine, yield
90% (Ref 3); and by the interaction of F_3CNO
with the eth complex of F_3CNOH, yield "good"
(Ref 4). It is stable to w, 10% HCl, and 10%
aq NaOH (Ref 2). The IR absorption bands are
listed in Ref 2
Refs: 1) Bell - not found 2) J. Jander &
R.N. Hazeldine, JCS 1954, 919 3) M.A.
Englin & A.S. Filatov, ZhObshKhKim 38, 1409
(1968) & CA 69, 66819e (1968) 4) V.A.
Ginsberg et al, ZhObshKhKim 38, 2505 (1968)
& CA 70, 57065s (1969)

Nitromethane (NMe). Nitromethan (Ger),
Nitrométhane (Fr), Nitrometano (It & Sp),
Nitrometan (Russ & Pol); CH_3NO_2; mw 61.04,
N 22.95%, OB to CO2 -39.3%, to CO -13%; a
liq, colorf when pure, coml grades are pale yel-
low, mp -28.55° (Refs l & 32), bp after dry-
ing over Ca chloride and distn 100.85-1.05°
(Ref 4), 101.20° (Ref 32); d at 20°, 1.13816
g/cc (Ref 32); RJ at 20°, 1.38149 (Ref 40);
visc at 25°, 0.632 centipoise; the driest samples
have the highest visc (Ref 17); CA Registry
No 75-52-5

Historical. NMe was first prep'd by Victor Meyer
who treated Me iodide with Ag nitrite and
obtained a 90% yield (Ref 2). This proc came
to be known as the Victor Meyer reaction (Ref
50). It has also been prep'd by the action of Me
sulfate on K nitrite (Ref 3). In the Victor Meyer
reaction the ratio of NMe to Me nitrite obtained
was found to be dependant upon solv, temp, and
the reagents used (Ref 5)
Preparation. Lab scale: To 500g of chloro-
acetic acid and 500g of cracked ice is added
enough cold 40% NaOH (ca 360cc) to make the
soh alk to phenolphthalein as the temp is held
below 20°. This soh is mixed with 365g of
Na nitrite in 500cc of w and the mixt heated
in a 3E round bottom flask fitted with a therm
dipping into the liq and an efficient condenser
set for downward distn. The soh is heated
gently until gas is evolved (ca 80°). The heat is
removed and the reaction proceeds spontane-
ously as the temp rises to ca 100° and the
NMe/w azote trope distils over at 90°. After the
reaction subsides, heat is applied until the temp
reaches 110° and NMe evolution ceases. About
113cc of NMe and 370cc of w are obtained. The
w is mixed with 3/4 its wt of NaCl and distd to
give 10-12cc of NMe. The crude NMe is dried
over anhyd Ca chloride and redistd to give
115-25cc of pure NMe, bp 98-100°, yield 35-
38% (Ref 11)

NMe is now commercially available and is prep'd
by the vapor phase nitration of methane at a
ratio of 9 moles of methane to 1 mole of nitric
acid at 475° and a residence time of 0.18sec
(Ref 12); or by the similar nitration of aliphatic
hydrocarbons (Ref 8). Other preps are from
Me sulfate and Na nitrite (Ref 26); by the oxidn
of Me amine with dinitrogen trioxide in the gas
phase or in methylene chloride, yield 27%
(Ref 28); and by the passage of Me chloride
into hot aq Na nitrite and Na carbonate in an
efficient column, yield 60% (Ref 28). Comm
NMe was purified for conductivity and other
measurements by the following procedure: The
NMe was distd, dried over anhyd Ca chloride,
and redistd. During the final distn the distill-
ate was passed thru a conductivity cell and the
fractions with the lowest conductivity saved.
The lowest obtained was 0.15 x 10^-7mho (Ref 6)
Chemical Reactions. For a review of the re-
actions of NMe see Ref 10. A brief list of its
principal reactions follows:
1) It is readily reduced to Me amine, and a
number of chem, catalytic, and electrochem
procedures have been used (Ref 10). 2) In most
cases the redn can be stopped at the hydroxyl-
amine stage to give N-Me hydroxylamine (Ref
10). 3) The action of strong acids on salts of
NMe gives derivs of formaldehyde (Ref 10).
4) Na hydroxide first forms the Na salt of NMe,
then the Na salt of methazonic acid, and finally
the Na salt of nitroacetic acid (Ref 10). 5) With
Hg(II) chloride is formed first the Hg salt of NMe
which rearranges and dehydrates to MF (Ref 10).
6) NMe is readily halogenated in the presence
of base to give halonitromethanes (see below).
7) It undergoes many condensation and addition
reactions with carbonyl compds, active methyl-
en compds, and activated oleins (Refs 10, 43,
46 & 51). 8) It reacts with formaldehyde to
form (HOCH_2)_2CNO_2, trivial name NIB-glycer-
ol. This is a large volume industrial process
(Refs 1 & 7). 9) Treatment with acrylonitrile in the presence of a trace of Na methoxide gives (NC6H5CH2)2CN=O (Ref 45). For details of the compds prep'd from NMe see in the Encycl under the individual compds.

**Analytical.** A diagnostic test to distinguish among RCH2NO2, R2CHNO2, and R3CNO2 is to treat the compd with nitrous acid. The first gives a red color, the second a blue color, and the third remains colorless (white). The test is called the red, white, and blue test (Ref 10).

The polarographic analysis of NMe was studied in buffered solns. The half wave potential was found to vary with pH, hence the necessity of using a buffered soln (Ref 22). Gas chromatog retention times for NMe at 50–90° and 110–50° are listed in Ref 38, various supports and stationary phases were used. Small amts were, quantity detd by coupling with p-diazobenzene-sulfonic acid and dsg the colored prod spectrophotometrically (Ref 37)

**Azeotropes.** NMe forms an azeotrope with w contg 76.4% NMe, bp 90° (Ref 40). It forms azeotropes with a large no of org liqs (Refs 1, 109 & 25).

**Brisance. Sand Test.** 8.1g of sand were crushed/g of NMe (Ref 36)

**Card Gap Test.** Results are given on NMe and mixts of NMe with TeNMe. A mixt having a slightly neg OB gave the highest value of 75 cards (Ref 35). Another gap test is given in Ref 22; with a donor charge of 50g of PETN/Mn 95/5 the max gap for deton transfer was found to be 3mm

**Critical Diameter.** The crit diam for deton propagation in iron tubes is 25mm, in brass 7mm (Ref 31)

**Detonability.** Some conditions under which deton of NMe has been observed are: 1) When subject to shock in heavy walled containers in large vol, as tank cars and trucks. After two disasterous exps of NMe in tank cars, its shipment in bulk was forbidden by the ICC (Ref 34). 2) It can be deton by the sudden impact of high press air, or by high press flow thru contractions in piping (Ref 15). 3) Intro of NMe at high press into lines contg air can result in deton, probably due to adiabatic comprsn of the entrapped air (Ref 16, p 24). The effect of a number of additives on the sensy of NMe to initiation with a No 8 blasting cap was examined and several were found to be effective at levels of 5–10% (Ref 16, p 31). Additives which can H-bond to the NMe molecule were found to be especially effective as sensitzers. Some are w, nitric acid, and sulfuric acid; however, phosphoric acid gave erratic resuts (Ref 16, p 11)

**Detonation Rate.** In glass tubing 1/32inch in diam, 6210m/sec (Ref 36); in iron tubing, 6280m/sec; in brass tubing, 6060m/sec (Ref 31); and in stainless steel tubing 3/16inch in diam, 20,000feet/sec (Ref 14, p 1)

**Dipole Moment.** In vapor phase 3.54 debye units (Ref 9)

**Explosion Temperature.** At 430° it expls in 5sec (Ref 36). The crit temp for expl was found to be 599°F and the crit press 915psi (Ref 52).

Pure NMe under air or N was found to deton betw 500 and 720°F. Ten additives in varying concns were tried as desensitzers, but there was no change in the temp range (Ref 14)

**Flammability.** The flash point is 112°F (Ref 50); in the Abel-Pensky app it is 35–37°F; and by Marcusson's method it is 42–43°. The autoignition point by Constam & Schlaepfer's method was found to be 440°F (Ref 48)

**Fricion Pendulum.** It is unaffected by the steel or fiber shoe (Ref 36)

**Heat Capacity.** The eqn Cp = 0.4209 - 0.0076 + 0.5605t° is valid over the range 15–75° (Ref 36).

Other eqns and data for heat capacity calculs are given in Ref 48

**Heat of Combustion.** At 25° it is 175.25 ± 0.18 kcal/mole (Ref 17)

**Heat of Formation.** -21.28 kcal/mole (Ref 17)

**Heat of Vaporization.** 149 kcal/g (Ref 36)

**Heat Tests.** Effect of heat: at 300° NMe has a half-life of 30 days, at 350° it decomposes slowly, at 350–400° it decomposes slowly and completely, above 400° an autocatalytic decomp sets in resulting in deton; however, it may detonate unexpectedly at any temp above 300° (Ref 16)

**Impact Sensitivity.** On BM app 100cm (Ref 36)

**Power, Ballistic Mortar.** 134% of TNT (Ref 36)

**Traufl Test.** 110–27% of PA (Ref 36 & 48)

**Rifle Bullet Impact Test.** Unaffected (Ref 36).

In Ref 15, however, it was reported that NMe, when stored in drums, is deton by the impact of fire from a 0.30 cal MG when firing AP ammo, and set on fire when tracers are used

**Solubilities.** In w, 9.5ml/100ml; sol of w in NMe
is 2.2ml/100ml (Ref 40). It is miscible in alc
eth, and dimethylformamide (Ref 50). An
extensive table of miscibilities of NMe in org liqs
is given in Ref 40, p 864a
Spectra. Infrared. The IR spectrum is given in
Ref 19
Nuclear Magnetic Resonance. There is a single
proton peak at 244r (Ref 42)
Ultraviolet. There is a n-π* transition at 3636
cm⁻¹ (Ref 41)
Thermal Decomposition. The therm decomp
was studied betw 380 and 430° and found to be
homogeneous and apparently 1st order. The
products were complex and included nitric
oxide, methane, carbon monoxide, and w plus
small ams of ethane, ethylene, and nitrous
oxide (Ref 23)
Toxicity. Vapors of NMe are irritating to the
lungs. Prolonged contact produces loss of ap-
petite, nausea, diarrhea, and damage to the liver
and kidneys. The lethal concn in air for guinea
pigs is 1000ppm (Ref 50). The systemic toxicity
is high when inhaled or ingested (Ref 47).
The LD50 in mice is 950+122mg/kg; in rats 900±
80mg/kg. The MAC in drinking w is 0.005mg/l
due to the formation of chloropirin during
chlorination of the w (Ref 49)
Uses. NMe has been used as a solv, a chem in-
termediate, a propellant, and an expl. For a review
see Ref 10. It is used as a solv for the detn of the
HMx content of RDX by differential refracto-
metry (Ref 27). It is used as a solv in the prep
of fine particle size NC (plastisol NC) (Ref 53).
It was first considered for use as a liq monopo-
plnt by L. Crocco (Ref 20), but it never lived up
to its expectations because of these disadvan-
tages: 1) It is difficult to ignite. The addn of
oxygen eases this problem, but expls occur on
ca 25% of ignitions (Ref 15). 2) It tends to ex-
plode erratically when pumped at high press,
or when used to cool the walls of a rocket cham-
ber (Ref 33). A gel contg 10–15% NC has been
patented as a rocket fuel or an expl (Ref 30).
Another gel of NMe with 3% Gengel guar gum
has been proposed for use as an expl for crater-
ing, excavation, and other blasting work. The gel
has a differential thermal analysis endotherm at
120° due to evap of the NMe; and a gap test of
0.8–3.1mm (0.38mm for pure NMe) (Ref 54).
Gelled NMe is compared with AN/fuel oil as a
blasting expl in Ref 55. Advantages of AN/fuel
oil are that it is cheaper and easier to handle and
store; advantages of gelled NMe are that it is
denser, has a higher detonation velocity, and has
a higher energy output/cc. NMe can be used as a
motor fuel, both spark ignition and diesel,
either alone or mixed with gasoline. For a review
of this use see Ref 39
Salts. HgOH+ salt. It is prepd from the Na salt
and Hg(II) chloride. The Pb block expansion test
gives 7.5cc/2g, but it has little effect in the Pb
plate test (Ref 13)
Li salt. It is claimed as a corrosion inhibitor for
lubricants (Ref 24)
Na salt. It is prepd by the action of Na hydride
on NMe in anhyd eth (Ref 44). It is sensitive and
when dry will burst into flame when thrown
onto w (Ref 50)
PhHg+ salt. Prep by the reaction betw PhHgOH
and NMe, yield 73.7%; mp 172–73° (with igni-
tion) (Ref 29)
K salt. Prep by the action of K hydride on
NMe in anhyd eth (Ref 44)
Tl+ salt. Prep by the addn of TiOH to NMe,
yield 85%; decompd without melting and could
not be detonated by impact (Ref 18)
Refs: 1) Beil 1, 74, (19); [106] & (100)
2) V. Meyer, Ann 171, 1 (1874)
3) P. Walden, Ber 40, 3214 (1907) & CA 1, 2689 (1907)
4) J.W. Williams, JACS 47, 2644 (1925)
5) R.P. Reynolds & H. Adkins, JACS 51, 279
6) C.P. Wright et al, JCS 1931, 199
7) I.M. Gorski & S.P. Makarow, Ber 67, 996
(1934)
8) H.B. Hass et al, IEC 28, 339 (1936)
9) L.G. Groves & S. Sugden, JCS 1937, 158
(1938)
11) OrgSyn (Coll Vol 1, 1941), p 401
12) T. Boyd & H.B. Hass, IEC 34, 300 (1942)
13) Blatt, OSRD 2014 (1944)
14) K. Kaplan et al, “Thermal and Shock Sensitivity of Nitro-
methane”, JPL Progress Report 1-35, Contr No
W-535-AC-20260 (26 Dec 1945)
15) F. Bellinger et al, IEC 40, 1320 (1948)
16) D.M. Griffin, “The Thermal Stability of Nitromethane”,
JPL Progress Report 9-24, Contr No
W-04-200-ORD-1482 (8 Dec 1948)
17) D.E. Holcomb & C.L. Dorsey, IEC 41, 2788 (1949)
18) H. Gilman & R.K. Abbott, Jr, JACS 71,
659 (1949)
Nostrand, NY (1949), p 190
20) L. Crocco, ARSJ 20, 32 (1950) & CA 44, 11057d (1950)

NITRO HALOGEN DERIVATIVES
OF METHANE

Fluoronitromethane. FCH2NO2, mw 79.04, N 17.73%; OB to CO2 = 20.24%; a colorless liq, bp at 125–30mm, 57–62°; CA Registry No 21824-09-9. It has been prepd by the hydrolysis of diethyl fluoronitromalonate, followed by decarboxylation, yield 5–32%, yields are erratic. IR peaks are at 6.27, 7.27, 7.37 and 8.8μ. It is stable only at 0–5°.

Refs: 1) Beil – not found 2) J.P. Lorand et al, JOC 34, 4176 (1969)

Difluoronitromethane. F2CHNO2, mw 97.03, N 14.44%; OB to CO2 = 8.24%; a volatile liq, bp 43–3.5°; d at 20°, 1.4600g/cc; RI at 20°, 1.3175 (Ref 5); CA Registry No 1493-03-6

It has been prepd by the reaction of Ag nitrite with difluorodicromethane (Ref 2); by the decarboxylation of difluoronitroacetic acid with anhyd K fluoride (Ref 3), or anhyd K carbonate, yield 46% (Ref 5); or by heating 1,1-difluoro-4-methyl-1-nitro-2-trifluoromethyl-4-penten-2-ol to 100° with a trace of K hydroxide, yield 82% (Ref 4).


Trifluoronitromethane. (Fluoropicrin) F3CNO2, mw 115.02, N 12.18%; a colorli gas, bp =–1° (Ref 3); CA Registry No 335-02-4

It was first prepd in low yield by the action of Cl trifluoride on bromodifluoronitrosomethane and by the oxidn of trifluoronitromethane with Pb dioxide (Ref 2). The Pb dioxide oxidn of the nitroso compd was repeated by Hazeldine who obtnd a 37% yield (Ref 3). This oxidn has also been carried out using dimanganese heptoxide (Ref 3). 30% hydrogen peroxide in a sealed tube (Ref 4); and activated C (apparently contg adsorbed O2) in a sealed tube at 150° for 1
hour, yield 7% (Ref 5). It has also been prepd by the action of Sb trifluorodichloride on chlorodifluoronitromethane (Ref 3)
Spectra. The IR spectrum and band assignments are given in Ref 6; in the UV there is a n-π* transition at 35842 cm⁻¹ (Ref 7)
Use: A mixt of 0.151 to 1 part of ammonia is claimed as a lig rocket monoprop, Isp 218 lb-
sec/lb (Ref 8)
Refs: 1) Beil 1, 105 2) W. Hückel, Nach-AkadWissGöttingen, Math-PhysikKlasse 1946, 36 & CA 43, 6793d (1949) 3) R.N. Hazel-
Chloronitromethane. This article supplements the material in Vol 3, C258-Rff under Chloro-
methane and Derivatives. Bp at 60mm 58–60°, d at 20° 1.472g/cc, RI at 20°, 1.4450 (Ref 3); CA Registry No 1794-84-9
It is prepd by the action of w on 2,3-
dichloro-3,3-difluoro-2-nitropropionyl chloride at 45–50° for 4 hours, yield 61% (Ref 3). It undergos the ter Meer reaction with Na ni-
tite to give dinitromethane (Ref 2). The IR and Raman spectral peaks are assigned in Ref 6. The pKₐ at 25° was found to be 7.20 (Ref 4).
In polarographic analysis it gives two breaks in the curve, indicating a two electron reduction probably by the eqn CICH₂NO₂⁺2e⁻ = CH₂NO₂⁻ +Cl⁻ (Ref 5)
Refs: 1) Beil 1, 106 2) H. Feuer, "Recent Advances in the Chemistry of Polynitro Compounds" in T. Urbanski, Ed, "Nitro Com-
5) J. Armand, BullFr 1966, 546 & CA 64, 17040e (1966) 6) P. Gluzinski & Z. Eck-
stein, SpectrochimActa 24A, 1777 (1968)
Chlorofluoronitromethane. CICHNO₂, mw 113.49, N 12.34%; BO to CO₂ -7.05%; bp 79–81°, d at 20° 1.532g/cc. RI at 20° 1.3840 (Ref 2). It is prepd by the decarboxylation of chlorofluoronitroacetic acid with hot w (Ref 3), or anhyd K fluoride (Ref 2). Its pKₐ in w is given as 10.14 in Ref 4
Dichloronitromethane. CIC₃F₂NO₂, mw 131.48, N 10.66%; bp 24–25° (Ref 2). It is prepd by the oxidn of the nitroso compd with dimanganese heptoxide, yield 15% (Ref 2), or by the interaction of difluoroazide with nitril chloride, yield 15% (Ref 3)
Refs: 1) Beil 1, 106 2) R.N. Hazelidine, JCS 1953, 2075 3) R.A. Mitch, JHetero-
cyclicChem 1, 233 (1964)
Dichloronoronitromethane. This article supplements the material in Vol 5, D1213-R under Dichloro-
methane and Derivatives. In polarographic analysis it shows a complex curve indicating two 2-electron reductions giving finally NMe and two Cl ions (Ref 1). Its pKₐ at 25° was found to be 5.99 (Ref 2)
Trichloronitromethane. This article supple-
ments the material in Vol 3, C256-R under Chloroform and Derivatives; CA Registry No 76-06-2. The IR spectrum and assignment of peaks are given in Ref 2; and in the UV there is a n-π* transition at 35907cm⁻¹ (Ref 3).
A procedure is described in Ref 5 for its spectrophotometric dttn in w. The thermodynamic props are calc'd in Ref 4
Bromonitromethane. This article supplements the material in Vol 2, B312-R under Bromo-
methane and Derivatives; CA Registry No 563-70-2. The IR and UV spectra are given in Ref 3. In polarographic analysis a two electron reduction to CH₂NO₂⁻ and Br⁻ is indicated (Ref 4). It can be quanly dttn by treatment with concd sul-
furic acid, then resorcinol, to give a colored complex which can be measured spectrophotometrically (Ref 2).

4) J. Armand, BullFr 1966, 547 & CA 64, 17040e (1966)

Bromodifluoromethane. BrCF₂NO₂, mw 175.94, N 7.96%; CA Registry No 354-42-7. It has been patented as an insecticide, fungicide, and nematicide


Bromodichlororomethane. BrCCl₂NO₂, mw 208.86, N 6.71%; bp at 22mm, 52°; d at 20°, 2.073g/cc. It is prepd by the action of 3p of Cl to one p of Br on NMe in basic soln, yield 33.2%


Dibromonitromethane. Br₂CHNO₂, mw 218.86, N 6.40%; a liq; bp at 13mm, 58.5–60° (Ref 2);
Rl at 25°, 1.5757 (Ref 4); CA Registry No 598-91-4. It was first prepd by the action of Br on bromonitromethane in basic soln (Ref 2), and later by the similar bromination of nitroacetamide (Ref 3). In polarographic analysis a two electron reduction to BrCHNO₂⁻ and Br⁻ is indicated (Ref 5).

Salts, Ammonium Salt. It is formed with Amm bromide by the action of liq ammonia on dibromonitromethane. The crude salt mixt is obtd as a yellow powd which gives free dibromonitromethane by the action of aq hydrobromic acid (Ref 4)

K salt. It is obtained as an orange powd which decomps suddenly on heating with formation of K bromide, but does not deton (Ref 3).


Dibromodifluoromethane. FCB₃NO₂, mw 236.86, N 5.91%. It is claimed to reduce hydrocarbon emissions from automobile exhaust when added to the fuel at 3.3% by vol.


Chlorodibromonitromethane. ClCB₃NO₂, mw 253.30, N 5.53%; a heavy oil; bp at 22mm, 67–69°; d at 25°, 2.398g/cc (Ref 3). It is prepd by the action of Br on chloronitromethane in aq K hydroxide (Ref 2), or by the action of 3p of Cl to one p of Br on NMe in basic soln, yield 35.4% (Ref 3).


Tribromonitromethane. This article supplements the material in Vol 2, B312-L under Bromoform and Derivatives; CA Registry No 464-10-8. The IR and UV spectra are given in Ref 4. In polarographic analysis a two electron reduction to Br₂CNO₂⁻ and Br⁻ is indicated (Ref 5). It adds to olefins to form 1,1,1-tribromo-2-nitroalkanes. The authors found that it is the only halonitroalkane to react in this way (Ref 3). When added to liq ammonia it forms a mixt of the Amm salt of dibromonitromethane and Amm bromide (see above) (Ref 2).


Iodonitromethane. ICH₃NO₂, mw 186.95, N 7.49%; OB to CO₂ -8.56%, an unstable, lacratory oil, odor unpleasant (Refs 2 & 3); CA Registry No 25538-43-6. It is prepd by the action of Ag nitrite on methylene iodide in the presence of a trace of I (Ref 2), or by the action of I on NMe in cold alkali (Ref 3). It is reduced electrolytically to iodide and NMe (Ref 4). A Na salt has been prepd as a white solid which expels on heating (Ref 2).


Dinitromethane (DNMe). CH₂(NO₂)₂, CH₂N₂O₄, mw 106.04, N 26.42%, OB to CO₂ +15.09%. It
is stored and handled in the form of salts, but has recently been obtd as an unstable oil, mp -15°C (Ref 3); bp at 4mm, 39–40°C; d at 20°C, 1.524/g/cc, RI at 20°C, 1.4480 (Ref 16); CA Registry No 625-76-3. It was first prepd by the action of aq AAm sulfide on bromodinitromethane (Ref 2); and by the action of cold concd sulfuric acid on the di-K salt of sym-dinitroethane (Ref 4), isolated as the K salt. It is best prepd by the reduction of dibromodinitromethane with As trioxide in cold aq K hydroxide and isolated as the K salt (Ref 3). The pure material has been regenerated from the K salt by treatment with anhyd hydrogen fluoride in abs eth (Ref 16).

Ionization. The pK_a at 25°C in w is 3.60, 50% aq et alc 4.11, et alc 7.5, and me alc 7.2 (Ref 17). Reactions. It reacts with benzenediazonium chloride to give yellow crystals, mp 75°C with gas evolution, whose structure was first thought to be (PhN-N)_2C(NO_2)_2 (Ref 3). More recently the reaction with p-nitrobenzenediazonium fluoroborate was examined in greater detail (Ref 11). The first prod isolated was the hydrazone O=N=N=N=O, mp 120–25°C with decomp. It degrades when heated on a spatula, and its solns decomp slowly in the cold and more rapidly on heating, with evolution of oxides of N. From the mother-liquor was obtained another compd, mp 164°C, which was considered to be a meso-ionic compd:

For a discussion of these type compds see Ref 12. The chemistry and technology of DNMe has been reviewed in Ref 9 with emphasis on its use as an intermediate for the prepn of nitropolymers, especially thru 2,2-dinitro-1,3-propanediol (code name A-diol).

Spectra. The UV spectra in w, acid, and base are given in Ref 5. The proton nuclear magnetic resonance spectrum shows a sharp singlet at 3.90ppm from tetramethylsilane (Ref 15).

Salts. Ammonium Salt. Obtained as bright yellow fine needles, exp at 105°C (Ref 3). It is completely ionized in w at 25°C (Ref 20).

Cs Salt. Its IR and UV spectra are given in Ref 19.

Li Salt. Its IR spectrum is given in Ref 13.

HgCl^+ Salt. It is prepd by the action of Hg(II) chloride on the K salt in water (Ref 6).

Phenylhydrazine Salt. It is prepd by the action of phenylhydrazine on dinitromethane in anhyd eth and obtd as intense yellow needles, mp 101°C with gas evoln (Ref 3).

Piperidine Salt. The ionization constant in water at 25°C is 3.37±0.01 (Ref 20).

K Salt. DNMe is stored and handled as the K salt which is obtd as brown-yellow feathery crystals, exp at 218°C (Ref 4). It is also prepd by the action of excess K cyanide or K thiosulfate on dibromodinitromethane (Ref 7). Best lab prepn: K nitrite (25g) in 40ml of water is added to 24g of chloronitromethane in 50g of me alc at 0°C. To this soln is added with good stirring 16.5g of K hydroxide in 50g of me alc as the temp is held between 0 and -5°C. The stirring is contd for 5 hours, the pptd solid filtered off, and recrystd from w to give 8.4g of K dinitromethane, yield 23.3%, exp at 200°C (Ref 8). More recently it is conveniently prepd on a lab and comml scale by the interaction of NMe and Na nitrite with a Ag salt, most commonly the nitrate. This reaction, developed by Shechter and Kaplan of the Purdue Research Foundation, is called the Shechter-Kaplan reaction (Ref 14). The IR spectrum is given in Ref 13. The ionization constant in w at 25°C is 2.26±0.01 (Ref 20). It readily adds to activated olefins (Ref 10).

Rb Salt. Its IR and UV spectra are given in Ref 18. The ionization constant in water at 25°C is 0.60±0.004 (Ref 20).

Ag Salt. It is formed from the K salt and Ag nitrate in w, decomp at 135°C (Ref 3). The IR and UV spectra are given in Ref 18. It reacts with Me iodide to give 1,1-dinitroethane (Ref 3).

Na Salt. The IR spectrum is given in Ref 13. It is estimated to be 100% ionized in w at 25°C (Ref 20).

Refs: 1) Beil 1, 77, (24), [44], [115] & (107) 2) S.M. Losanitsch, Ber 16, 51 (1884) 3) P. Duden, Ber 26, 3003 (1893) 4) R. Scholl & A. Schmidt, Ber 35, 4288 (1902) 5) A. Hantzsch & K. Voigt, Ber 45, 112 (1912) 6) W. Prager, Monatsh 33, 1285 (1912) & CA 7, 589 (1913) 7) R.A. Gotts & R. Hunter,
Halogen Dinitro Derivatives of Methane

All 14 possible halogen derivs of dinitromethane have been reported in the literature. They are sensitive to friction, shock, and impact, as well as being toxic and skin irritants (Ref 5).

Fluorodinitromethane. FCH(NO$_2$)$_2$, CHF(NO$_2$)$_2$, CHF$_2$N$_2$O$_4$, mw 128.04, N 21.88%, OB to CO$_2$: 18.74%, fr p -24.5$^\circ$, bp at 20mm 35-38$^\circ$, d at 20$^\circ$, 1.5955 g/cc; RI at 20$^\circ$, 1.4054 (Ref 4); pK$_a$ at 20$^\circ$ 7.70 (Ref 2); CA Registry No 7182-87-8. It is prep'd by the fluorination of the Ammi salt of dinitromethane at 2-3$^\circ$ in solution, yield 90% (Ref 4); by the action of H$_2$O peroxide and K hydroxide on fluoro-nitroform in methanol; or by the fluorination of the K salt of ethyl dinitrocate (Ref 5).

Hg Salt. It is prep'd by the action of Hg(II) monoxide in ether on the free nitro compd, yield 86%, mp 147$^\circ$ (Ref 6). It reacts with K hydroxide or K iodide to give the K salt of fluorodinitromethane, and with H chloride or H$_2$O to regenerate the free nitro compd (Ref 3).


Difluorodinitromethane. F$_2$C(NO$_2$)$_2$, CF$_2$N$_2$O$_4$, mw 146.03, N 19.19%; bp 34$^\circ$, d at 10$^\circ$, 1.5644 g/cc; RI at 10$^\circ$, 1.3640 (Ref 4); CA Registry No 1185-11-1. It is prep'd by the reaction of di-N- tetroxide with difluorodiazirine (Ref 2); by the fluorination of a mixt of K nitroform and Na fluoride at -12 to -6$^\circ$ in a Cu vessel (Ref 4); or by the action of anhyd K fluoride on fluoro- nitroform in sulfuric acid at 150$^\circ$, yield 58.7% (Ref 5). A mixt of 0.249p to one p of ammonia has been claimed as a liq rocket propellant (Ref 3).

Chlorodinitromethane. This article supplements the material in Vol 3, C259-L under Chloro- methane and Derivatives; CA Registry No 912-13-1. Its pK$_a$ in w at 20$^\circ$ is 3.53-3.80 (Refs 1 & 3). The K salt has a mp of 85$^\circ$ with decompn (Ref 2). The Hg salt is prep'd from chlorodinitromethane and the Hg salt of fluoro- dinitromethane. It reacts with aniline to form PhNH(NO$_2$)$_2$Cl, yield 59.1%, mp 125$^\circ$ with decompn (Ref 4).

Chlorofluorodinitromethane. FCCI(NO$_2$)$_2$, CClF(NO$_2$)$_2$, CClF$_2$N$_2$O$_4$, mw 158.49, N 17.68%; OB to CO$_2$: 20.19%, bp at 752mm 85-87$^\circ$; d at 20$^\circ$, 1.6162 g/cc, RI at 20$^\circ$, 1.3992 (Ref 5); CA Registry No 19845-51-3. It is prep'd by the action of di-N- tetroxide on chlorofluoronitroacetic acid in an autoclave at 80-90$^\circ$ (Ref 3); by the action of Li...
chloride in dimethylformamide on fluoronitroform; yield 35\% (Ref 4); or by the action of Cl in anhyd enth on the Hg salt of fluorodinitromethane, yield 72\% (Ref 5). The thermal decompn has been studied betw 170 and 240\°. The plot of log k vs 1/T was found to be a straight line from which the activation energy was calcd as 41.5 kcal/mole (Ref 2).


**Dichlorodinitromethane.** This article supplements the materials in Vol 5, DI123-R under Dichloromethane and Derivatives; bp at 50mm, 54–56\°; d at 20\°, 1.6643g/cc; RI at 20\°, 1.5460 (Ref 2); CA Registry No 1587-41-3. It is prepd by refluxing trichloroethylene with a 3 mole excess of 70% nitric acid (Ref 1); or by the action of Cl on the K salt of dinitromethane inaq K hydroxide (Ref 2). The thermal decompn between 115 and 150\° was found to be 1st order and homogeneous, the plot of log k vs 1/T gave a straight line (Ref 3). It is a useful herbicide for water plants (Ref 1).


**Bromodinitromethane.** This article supplements the materials in Vol 2, B312-R under Bromomethane and Derivatives; the pHK in w at 20\° is 3.47–3.60 (Revs 4 & 6); in the UV the lmax is at 385mu (Ref 6); CA Registry No 996-67-8. The Amm salt is formed by the action of liq ammonia on dibromodinitromethane (Ref 2). The K salt is a yellow solid, mp 152\° with decompn (Ref 5). It is formed by the action of phenylhydrazine inaq K hydroxide on dibromodinitromethane (Ref 2)


**Bromofluorodinitromethane.** BrCF(NO2)2, CBrF2O4, mw 202.94, N 13.81\%; bp at 40mm, 35–36\°; d at 20\°, 1.8722g/cc; RI at 20\°, 1.4351 (Ref 3); CA Registry No 22632-20-8. It is prepd by the action of Br in anhyd enth on the Hg salt of fluorodinitromethane, yield 76.4\% (Ref 3). The thermal decompn was studied betw 170 and 210\°. The plot of log k vs 1/T was a straight line from which the activation energy was calcd as 39.5 kcal/mole (Ref 2).


**Bromochlorodinitromethane.** BrCCl(NO2)2, CBrCl2O4, mw 219.41, N 12.77\%; a heavy oil, suffocating odor; mp 9.2–9.3\°, bp at 15mm, 75–76\°; d at 10\°, 2.0394g/cc; RI at 20\°, 1.4739 (Ref 4); CA Registry No 33829-48-0. It is prepd by the action of ac Cl on the K salt of bromodinitromethane (Ref 2), yields are improved by the addition of Na acetate (Ref 3)

**Revs:** 1) Beil 1, 78, [45] & [115] 2) S.M. Losanitsch, Ber 17, 848 (1884) 3) R.A. Gotts & L. Hunter, JCS 125; 447 (1924) 4) F.C. Schmidt et al, JOC 9, 421 (1944)

**Dibromodinitromethane.** Br2C(NO2)2, CBr2N2O4, mw 262.87, N 10.66\%; a heavy yellow oil, solidifies to white leaflets; fr p 6\°, mp 10\° (Ref 5); bp at 19mm, 78–80\° without decompn, expl at 158\° (Ref 6); d at 25\°, 2.3946 g/cc; RI at 20\°, 1.5215 (Ref 9). It is insol in w, miscible with et alc, and volat in steam (Ref 2); CA Registry No 2973-00-4. It has been prepd by the action of Br in w (Ref 7) oraq K hydroxide (Ref 11) on the K salt of dinitromethane; or by the introduction of Br vapors into a w soln of equal parts of the di-K salt of sym-tetrinitromethane and Na acetate (Ref 8). It is one prod isolated from the action of concd nitric acid on Br-contg cmpds such as ethylene dibromide (Ref 3), sym-trimethoxyaniline (Ref 2), p-bromo-phenol, and dibromo-p-toluidine (Revs 3 & 4).

The experimental details for its prepn from sym-trimethoxyaniline and concd nitric acid are given in Ref 10.

**Reactions.** For reactions see above under Dinitromethane and Bromodinitromethane

**Revs:** 1) Beil 1, 78 & [44] 2) S.M. Losa-

Iodonitromethane. ICH(NO₂)₂, CHN₂O₄, mw 231.96, N 12.08%, OB to CO₂ 10.33%; CA Registry No 29610-14-8. The K salt is formed by the action of I in aq K hydroxide on dinitromethane (Ref 2). It is obtained as yellow tablets which darken on standing and expl at 154° (Ref 3). The Ag salt is obtd as pale yellow leaflets which expl at 109–10° (Ref 3).

Refs: 1) Beil 1, 79 & [45] 2) S.M. Losanitsch, Ber 16, 51 (1884) 3) R.A. Gotts & L. Hunter, JCS 125, 443 (1924)

Fluoriodinitromethane. FCl(NO₂)₂, CFIN₂O₄, mw 249.96, N 12.08%; it is a liq which decomps slowly on standing in the dark, rapidly in light; bp at 27mm, 59–9.5°; d at 20°, 2.3541g/cc; RI at 20°, 1.4998 (Ref 3); CA Registry No 22632-21-9. It is prepd by the action of I in anhyd eth on the Hg salt of fluorodinitromethane, yield 74% (Ref 3). The thermal decompsn was studied betw 160 and 197°. The plot of log k vs 1/T gave a straight line from which the activation energy was calcd as 39.7kcal/mole (Ref 2).


Chloriodinitromethane. CCl(NO₂)₂, CClIN₂O₄, mw 265.42, N 9.05%; a colorl oil, characteristic odor; d at 12°, 2.1424g/cc; CA Registry No 40956-65-8. It is prepd by the action of aq Cl on the K salt of iododinitromethane

Refs: 1) Beil 1, [45] 2) R.A. Gotts & L. Hunter, JCS 125, 448 (1924)

Bromiodinitromethane. BrCl(NO₂)₂, CBrIN₂O₄, mw 310.88, N 8.01%; an unstable oil, odor disagreeable; CA Registry No 40956-66-9. It is prepd by the action of aq Br on an ice cold soln of the K salt of iododinitromethane

Refs: 1) Beil 1, [45] 2) R.A. Gotts & L. Hunter, JCS 125, 448 (1924)

Diododinitromethane. CH(NO₂)₂, Cl₂N₂O₄, mw 357.87, N 7.83%; an extremely unstable oil, odor disagreeable; CA Registry No 40956-64-7. It is prepd by the acidification of an ice cold soln of the K salt of iododinitromethane. It decomps on standing with the evolution of I and oxides of N

Refs: 1) Beil 1, [45] 2) R.A. Gotts & L. Hunter, JCS 125, 448 (1924)

Trinitromethane (Nitroform, TNMe). Trinitromethan or nitroform (Ger), Nitroforme (Fr); CH(NO₂)₃, CHN₃O₆, mw 151.04, N 27.82%, OB to CO₂ 137.0%; a colorl to pale yellow solid, a pale yellow liq; mp 26.3 ± 0.1° (Ref 46). It can also be obtained in a higher melting form, mp 50°, which was assumed by the authors to be the aci-form (Ref 15); bp at 22mm, 45–7° (Ref 16); d at 24.3°, 1.5967g/cc; RI at 24.3°, 1.44174 (Ref 11). The pH of a satd soln in w was measured with a glass electrode and found to be 0.6 (Ref 25, p 2); CA Registry No 517-25-9. The Hercules Powder Co of Wilmington, Del has been granted a trademark for Nitroform®. a synthetic w-insoluble compd for controlled release of N for agricultural use (Ref 40). This should not be confused with TNMe

Historical. It was first prepd by the action of nitric acid (d 1.52 g/cc) on acetylene (Ref 5), and this is the basis for one industrial process for mfg TNMe (Ref 10, 29 & 35). This reaction was first examined on a large scale in Ger during WWII, where it was used to prepare TNMe and TeNMe for use as intermediates for the prepn of exps (Ref 18).

Preparation. A continuous process is described in Ref 26 for its prepn from nitric acid and acetylene. Other prepns on both lab and industrial scales are by the action on Tetrinitromethane (TeNMe) of K hydroxide in aq glycerol (Ref 16), aq HOCH₂SO₃Na, or 30% aq H peroxide (Ref 19a) to give the K salt which is treated with sulfuric acid (Ref 16), syrupsy phosphoric acid (Ref 20), or best by passing gaseous HCl thru a suspension of the K salt in anhyd eth (Ref 19a). It has also been prepd by the action of nitric acid on malonamide,
yield 58% (Ref 34); Ac₂O (Ref 27); the di-K salt of dinitroacetate acid, yield 54% (Ref 28); or ethylene (Ref 12)

**Laboratory Preparation.** A soln of 168g of K hydroxide in 350ml of w is cooled to 5° and 120g of 30%aq H peroxide added with stirring. Next is added, with stirring, 189g of TNMe at a rate which keeps the temp at 20–5°. It is then allowed to rise to 30° over 15min, the bright yellow solid collected on a glass frit, washed with anhyd HCl, then anhyd eth, and air dried to give 100% of the K salt of TNMe. The salt is suspended in anhyd eth and anhyd HCl passed in until the yellow color disappears. The white ppt of KCl is filtered off and washed with anhyd eth. The eth is evpd from the filtrate and addnl washings at reduced press give 85–95% of crude TNMe which can be purified by sublimation (Ref 19a, p 79)

**Chemical Reactions.** TNMe is a strong acid and forms salts with metals and bases (see below). It readily reacts with formaldehyde to form trinitroethanol (Ref 16). It adds to activated double bonds, such as α,β-unsaturated carbonyl cmpds and vinyl ethers (Ref 19b).

It forms a complex with dioxane contg 2 moles of TNMe to one of dioxane, mp 44–4.5°, bp at 8 mm, 61–2° (Ref 19a, p 33). It reacts with aromatic diazonium salts to give cmpds of the type ArN⁺NC(NO₃)₂. The cmpds are relatively unstable and their expl props have not been examined (Ref 12). It reacts with N-hydroxymethyl cmpds to form adducts of the type RNH₂CH₂CN(NO₃)₂. The same cmpds are formed from TNMe, formaldehyde, and the amine; or from trinitroethanol and the amine (Ref 31). It forms complexes with N-contg heterocycles whose expl props have not been examined (Ref 42). It forms complexes with benzene and methylenbenzenes. The formation constants for these complexes vary from 8.46 for the benzene complex to 279.4 for the hexamethylbenzene complex (Ref 49)

**Analytical.** It can be titrated with std base to a salmon colored phenolphthalein endpoint; and can be quanty pptd fromaq solns with tetraphenylarsonium chloride; Kₛₚ of the complex in w is 6.9 x 10⁻³⁰ (Ref 22). This procedure can be adapted to the analysis of cmpds, such as bis(trinitroethyl) urea, which regenerate TNMe on alkaline hydrolysis. In an ion exclusion-partition chromatographic method for the sepn of acids, TNMe emerged from the column betw citric and itaconic acids (Ref 36)

**Impact Sensitivity.** On the BRL machine (1kg wt), using a noisometer to detect expls, the 50% expln height was found to be 218cm. A 50/50 mixt with kerosene had a 50% expln height of 130cm (Ref 21)

**Power by Ballistic Mortar.** 125–37% of TNT (Ref 24)

**Spectrum, Ultraviolet.** It shows a plain shoulder in eth, and in w shows a broad maximum at 3400Å (Ref 7)

**Stability.** It may be stored indefinitely at 0° in sealed glass ampules (Ref 20)

**Toxicity.** The toxic concs in air for mice are: LD (minimum) 0.7, LD₅₀ 0.8, and LD₁₀₀ 1.0mg/l; the max acceptable concn is suggested to be 0.0005mg/l (Ref 37). There is a large amt of toxicological info on the effects of TNMe in this Ref

**Uses.** It was found to be a poor gelling agent for NC (Ref 14). Its principal use is as an intermediate for the prep of other expl cmpds.

**Salts, Ammonium Salt.** Yellow needles from w (Ref 6). It is prep by the action of w or et alc on trinitroacetone (Ref 2), or by the action of ammonia on TNMe (Ref 6). The Qₐ was found to be 1108.6± 1.3cal/g. From this was calc the Qₐ as -47.3±0.2kal/mole at 1 atm and 25°, and the energy of the bond betw Amm and the nitroformate ion to be 24.8±0.7kal/mole (Ref 47). It is 100% ionized in w at 25° (Ref 50). It has been patented as an ingredient in high energy proplnts (Ref 32)

**Ba Salt.** Fine pale yellow cryts, prep by the action of Ba oxide on TNMe inaq glycerol (Ref 13). A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

**Ca Salt.** A complex with hydrazine is claimed as a proplnt ingredient (Ref 39)

**2,4-Dinitrophenylhydrazine Salt.** It is prepd by the addn of the hydrazine in iso-Pr alc to TNMe in the same solv, mp 120–23° (Ref 48)

**Guandidine Salt.** It was first prepd in Ger during WWI by the addn of a guandidine salt to the K salt of TNMe in w. The hydrate is obtained as needles, mp 122–24°, the anhyd salt mp 128°. Impact sensy (2.5kg wt) 50% expln height,
17 cm; deton vel at a loading d of 1.66 g/cc, 8200 m/sec; cryst d 1.643 g/cc; vacuum stablity: gas evoln 1.39 cc/g in 48 hours at 90°; mixed with Al powd. 1.70 cc/g in 48 hours at 90°. It detond after 30 hours at 100° (Ref 25)

**Hydrazine Salt.** Fine yellow crystals, mp 123° with decompn (Ref 25). It is prepd by the addn of hydrazine hydrate to TNMe in w (Ref 25), or by the addn of anhyd hydrazine to TNMe in iso-Pr alc (Ref 48). The crytst structure and X-ray diffraction pattern of the pure salt are given in Ref 45. Impact sensy (2.5 kg wt), the 50% expln height was found to be 10 cm (Ref 25). It is stable to 100° (Ref 48). It is claimed as an ingredient in a thixotropic propellant formulation (Ref 41)

**Li Salt.** A complex with 2 moles of hydrazine is obtained as an orange-yellow solid, mp 70° with decompn (Ref 39). It is claimed as an oxidizer in propellant formulations (Ref 39). It is 100% ionized in w at 25° (Ref 50)

**Hg Salt.** Colorl crystals, slightly sol in org solvs; prepd by the action of Hg oxide on an eth soln of TNMe (Ref 4). It reacts with olefins to form adducts contg one or two trinitromethyl groups, depending on reactant ratios (Ref 33). The ionization const in w at 25° is 6.04 x 10^-3 (Ref 50)

**Mg Salt.** It forms an orange-yellow complex with hydrazine, mp 88° with decompn, d 1.68 g/cc, impact sensy 11.7 cm (2 kg wt). The salt has been patented as a propellant ingredient (Ref 39)

**Methylamine Salt.** A yellow solid, mp 126–28° with decompn; ign temp 112°; vacuum stablity 1.64 cc/g of gas evolved at 60° in 2 hours, 2.04 cc/g at 60° in 48 hours (Ref 43). It has been patented as an expln ingredient (Ref 44) and a propellant ingredient (Ref 41)

**K Salt.** A yellow crytst solid, prepd by the action of basic K salts on TNMe in the presence of reducing agents (see also above under TNMe). Some which have been used are: K methoxide in me alc (this proc is subject to dangerouns explns) (Ref 8); K cyanide in me alc (Ref 23); a satd q soln of K ferrocyanide (Ref 9); or K nitrite in w, yield 80% (Ref 38). It has also been prepd by the action of K nitrite on dibromodinitromethane (Ref 13). Its expln temp is 97–98° (Ref 3); and its impact sensy, using a noisemeter to detect explns, was found to be 44.3 cm (50% expln height, 1 kg wt) (Ref 21). The soly in w and et alc was detd betw 0 and 60° (Ref 13). It is 100% ionized in w at 25° (Ref 50). It is claimed as a corrosion inhibitor when added at a level of 0.05–0.1% to liq rocket propulnts (Ref 30)

**Piperidine Salt.** Its ionization constant in w at 25° is 0.288 ± 0.001 (Ref 50)

**Rb Salt.** It is prepd from TNMe and Rb hydroxide in w, decomp in 157–59°. The ionization constant in w at 25° is 0.613 ± 0.003 (Ref 50)

**Ag Salt.** It is prepd by the action of Ag oxide on TNMe in eth, mp 100° (Ref 3). It reacts with benzyl halides to form trinitroethyil derivs (Ref 17). Explodes mildly on rapid heating (Ref 3)

**Na Salt.** It is prepd by the action of Na nitrite on TNMe in me alc or et alc (Ref 38). It is completely ionized in w at 25° (Ref 50). A complex with hydrazine is claimed as a propellant ingredient (Ref 39)


Halogen Derivatives of Trinitromethane
Fluorotrinitromethane. FC(NO_2)_3, mw 169.03, N 24.85%. A colorless to pale yellow liq, bp 84.2°, d at 20°, 1.795g/cc; RI at 25°, 1.3944; Q_f at 25°, -51.99kcal/mole (Ref 3); CA Registry No 1840-42-2. It has been prepared by the action of F in N 1:6 on a mixt of 20g of solid K salt of TNMe, 40g of K fluoride, and 50g of Cu turnings at -12 to -6° in a Cu vessel (Ref 4); by the action of 10% F in He on the K salt of TNMe in w, yield 48%, purity by gas chromatography 99.42 mole% (Ref 3); by the action of F on the Na salt of TNMe in aq Na hydroxide (Ref 5); or by the action of KF on TeNMe in dimethylformamide (Ref 6). It could not be detoned with a hammer blow (Ref 2). It is a useful oxidizer in monopropellants or hypersonic bipropellants (Ref 6). Calcd lsp with fuels as are as follows: 0.304:1 with ammonia, 265; 0.469:1 with hydrazine, 281; 0.151:1 with triptane, 270; 0.262:1 with acetonitrile, 267; 0.313:1 with me alc, 261; and 0.185:1 wt ratio with 1,2-bis(dimethylamino)propene, 271 lb-sec/lb (Ref 2). It does not react at ambient temp with acetonitrile, triptane, acet, me alc, benzene, nitrobenzene, and cyclohexane (Ref 2)

kas & K. Baum, JOC 33, 3080 (1968)

Chlorotrinitromethane. CIC(NO₃)₃, mw 185.46, N 22.65%. A very pale yellow oil, freezes to a white solid, insol in w, sol in org solvs (Ref 3). Its odor is penetrating and unpleasant, resembling chloropicrin; and it is a lacrymator (Ref 3). Mp 5.85° (Ref 8); bp at 9mm, 35° (Ref 3); d at 20° 1.6769g/cc (Ref 6); RI at 20°, 1.4471 (Ref 8); dipole moment at 25°, 2.17 debye (Ref 5); heat capacity 0.21cal/g/deg; Qₓ, 10.86kcal/mole; Qᵧ at 25°, -5.57 ± 0.18 cal/mole (Ref 8); CA Registry No 1943-16-4. It is prep'd by the action of Cl on the K salt of TNMe in ice cold eth (Ref 2), or in w (Ref 3); or by the slow addn of acet to a mixt of nitric acid and HCl (Ref 4). Its IR and UV spectra are given in Ref 7. It reacts with K hydroxide in w or et alc to give the K salt of TNMe (Ref 4). The thermal decomp was studied at 170° and 400mm. The decomp prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxides, C monoxide, C dioxides, cyanogen chloride, and Cl (Ref 9).


Bromotrinitromethane. BrC(NO₃)₃, mw 229.95, N 18.23%. A faintly greenish yellow liq; mp 9.5-10°; bp at 8mm, 59° (Ref 4); d at 20°, 2.0313g/cc; RI at 20°, 1.4808 (Ref 7); dipole moment at 25°, 2.56 debye (Ref 6); CA Registry No 560-95-2. It has been prep'd by the action of Br on TNMe in sunlight (Ref 2); in nitric acid (Ref 4); on the K salt of TNMe in ice cold eth, yield 90% (Ref 7); or on the Hg salt of TNMe in acet, yield 87% (Ref 5). It reacts with K hydroxide in et alc to give the K salt of TNMe (Ref 3), and with olefins to form 2-bromo-1-nitrate esters which can be hydroyzed to the bromoalcohols (Ref 8). The thermal decomp was studied at 170° and 400mm. The decomp prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxides, C monoxide, C dioxides, cyanogen bromide, and Br (Ref 9).


Iodotrinitromethane. ICl(NO₃)₃, mw 276.46, N 15.19%. Bright yellow leaflets, insol in w, sol in hot et alc, benzene, or ligroin (Ref 2); mp 55-56°; bp at 13mm, 48-8.5° (Ref 3); dipole moment 3.79 debye (Ref 4); CA Registry No 630-70-6. It is prep'd by the reaction betw I and the Ag salt of TNMe (Ref 2); or by the action of I on the K salt of TNMe in ice cold eth, yield 50% (Ref 5). It may expld violently on standing (Ref 3). It gives TeNMe on treatment with Ag Nitrite and the K salt of TNMe on treatment with Ag K hydroxide (Ref 2). It reacts with ethylene and cyclohexene to form 2-iodonitrone esters which react further to form ozonolides (Ref 6). The thermal decomp was studied at 170° and 400mm. The decomp prods were sepd by gas chromatography and identified by mass spectroscopy as N, nitric oxide, N dioxides, C monoxide, C dioxides, cyanogen iodide, and I (Ref 7).


Tetranitromethane (TeNMe). Tetranitromethan (Ger), Tétranitrométhane (Fr), Tetranitrometano (It), Tetranitrometan (Russ); C(NO₂)₄, mw 196.04, N 28.57%; OB to CO₂ +49%; a colorless pale yellow liq, freezes to a colorless solid. Its odor is described as pungent (Ref 21).

Pure TeNMe is said to be colorless, but becomes yellow on contact with w, due to hydrolysis to TNMe (Ref 5). Mp 14.2° (Ref 26); bp 125.7° (Ref 10); d at 25°, 1.62294g/cc; RI at 25°, 1.43822 (Ref 18). The dipole moment is essentially zero, indicating the structure to be symmetric, instead of (O₂N₃)CONO as had been postulated to account for its reactivity (Ref 18), CA Registry No 509-14-8

Historical. It was first prepd by the action of nitric acid on TNMe (Ref 2). This reaction is the basis of large scale prepns in which acetylene is nitratd to TNMe and the latter treated with an excess of nitric acid to give TeNMe (Ref 26). As stated above under TNMe, in Ger during WWII, the prepn of TeNMe by this process was scaled up for use as an intermediate and as a substitute for nitric acid in the V-2 rocket (Ref 26). A pilot plant was built at Newark, NJ for prodn using this procedure. It was destroyed by an exphil in 1953 and not rebuilt (Refs 33 & 44). Other prepns of lesser importance are by the action of Ag nitrate on iodotrinitromethane (Ref 3); by the action of 90% nitric acid and 25% oleum on malononitrile, yield 45% (Ref 40); by the action of mixed acid on a number of aromatic nitrocompounds, of which nitrobenzene, dinitrobenzene, and nitronaphthale gave the best yields (Ref 13a); and by the action of nitril chloride on salts of TNMe. The best yield, 95%, was obtained with the K salt (Ref 38). It is formed in small amts during the nitratin of toluene to prepare TNT (Refs 37 & 38), and has been held responsible for explns which have occurred in TNT mfg plants. It has been postulated that mixts of TeNMe and toluene, which are as sensitive as NG, have condensed in off gas lines and detonated (Ref 37). Crude TNT, therefore, contains varying amts of TeNMe which, being highly toxic, accounts for conflicting reports as to the toxicity of TNT (Ref 37). By the use of C¹⁴-labeled TNT, it was shown that 54.2% of the TeNMe came from the aromatic C attached to the Me group, 8.3% from each of the C atoms connected to nitro groups, 7.4% from each of the C atoms attached to H, and 6.1% from the Me group (Refs 37 & 38)

Laboratory Preparation. Anhydrous nitric acid (31.5g) in a 250ml 2-necked flask fitted with a dropping funnel and thermometer reaching to its bottom is cooled to 10°, and 51g of Ac₂O is added slowly at a rate which keeps the temp below 10°. After all is added, the funnel is removed and the flask allowed to warm slowly to room temp, allowed to stand a week, the contents poured into 300ml of w in a 500ml flask, and the TeNMe removed by steam distn. The lower layer of the distillate is sep'd, washed with dil alkali, w, and dried over anhyd Na sulfate; yield 57—65% (Ref 32). TeNMe should not be distd as it can expl with great violence, and distn residues are especially dangerous (Ref 46). A continuous process using this reaction is described in Ref 34. A similar prepn is by heating acetyl nitrate with acet ac or Ac₂O (Ref 4) Chemical Reactions. TeNMe gives TNMe or salts of TNMe under a variety of conditions (see above under TNMe). It is a mild oxidizing agent, converting hydroquinone to quinhydrone, N,N-dimethylaniline into crystal violet (Ref 8), and thiourea into (H₂NC(S)₂ (Ref 14). It is a nitrating and nitrosating agent (Ref 26), converting triethylamine into diethylnitrosamine (Ref 12). It is reduced to guanidine and ammonia with Zn (Ref 14) or Fe (Ref 13) andaq HCl

Analytical. A proc is described for the quant titrimetric analysis of TeNMe in nitric acid (Ref 35), and a spectrophotometric method is described in Ref 41 for the detn of small amts of TeNMe in air and w

Critical Diameter. The crit diam for deton propagation of TeNMe thickened with poly- (methyl acrylate) and loaded with up to 75% inert solids was detd and found to decrease with increasing solids loading. It was postulated that the solids acted as reaction foci ahead of the deton front (Ref 45)
Explosion Temperature. It does not expl below 360° (Ref 21)

Heat of Combustion. 102.9 kcal/mole (Ref 22)

Heat of Explosion. From a differential therm analysis exotherm at 310° the Qe at 227° was calculated to be 557 kcal/g (Ref 39)

Heat of Formation. -8.9 kcal/mole (Ref 22)

Impact Sensitivity. Described as “similar to TNT” (Ref 21). On BM app (2kg wt) the 50% expln height was found to be 100cm (Ref 25)

Shock Wave Sensitivity. A test is described to detn the shock wave sens of liq expls. A crit thickness is detd for which an impressed shock wave causes a deton. For TenMe this was detd to be 3mm. An eqn is developed to relate this thickness with other parameters such as press and deton vel (Ref 42)

Spectra, Infrared. The IR spectra in the gas, liq, and solid states are in Ref 30

Ultraviolet. \( \lambda_{\text{max}} \approx 275\text{nm}, \log e 2.2 \) (Ref 19)

Thermal Stability. At 100° it evolves acid fumes in 30min, at 135° there is no expln after 200min (Ref 21)

Toxicity. It is a lacrimary and irritates the skin mucous membranes, especially of the respiratory tract (Ref 26). Prolonged exposure to vapors causes damage to liver, kidneys, and other organs. Conc in air of 0.1ppm is fatal and 3.3ppm or higher are rapidly fatal (Ref 47, p 1156). Its threshold limit value in air is set at 1ppm (Ref 47, p 22)

Trauzl Test. 21.4% of TNT when pure (Ref 26); for mixts see below

Uses. It does not gelatinize NC (Ref 15). It improves the octane rating of diesel fuels (Ref 26). It decreases the polymerization rate of methyl methacrylate (Ref 24), and styrene (Ref 23), but does not inhibit the reaction. A review of its use as an oxidizer in rocket propants is given in Ref 33. TenMe gives yellow to orange colors with olefins and aromatic compds. This is used as a diagnostic test for the presence of these groups in org analysis (Refs 6, 9, 16, 17 & 29)

Explosive Mixtures with Organic Compounds. Mixts with org compds are more powerful and sensitive expls than TenMe. Those whose expl props have been detd are listed below:

Benzene. A mixt of 2 moles of TenMe and one of benz gave an expln temp of 163.3° (Ref 11)

An 87:13 mixt with benz gave a Trauzl test of 134% of TNT (Ref 26). Mixts of from 65 to 90% by wt in benz had a card gap test of over 300 cards, indicating them to be very sens (Ref 36). The sens of mixts with benz was found to be due to the formation and collapse of cavitation bubbles in the liq (Ref 43)

Ethylene Glycol. A 50% soln by wt had a card gap test of 270 cards (Ref 36)

Gasoline. Mixts with gasoline and diesel fuel were found to be powerful, but sens expls (Ref 26)

Hydrocarbons. Addn of metallo-org compds lowers the burning rate of TenMe/hydrocarbon mixts to the point where they are useful monopropnts (Ref 27)

Naphthalene. A mixt of 2 moles of TenMe to one of naphthalene gave an expln temp of 160.4° (Ref 11)

Nitromethane. A mixt of 4 moles of NMe to one of TenMe gave a maximum expansion of 30.62 in the Pb block expansion test (Ref 20). A mixt contg 40% TenMe had a card gap test of 75 cards (Ref 36)

Paraffins. Mixts of 10–40% paraffins and 69–90% TenMe are liq expls which are readily detoned by expl shock, but are resistant to mech shock (Ref 28)

Sodium Methoxide. TenMe expls violently in its presence (Ref 7)

TNT. The power by BallPend of mixts with TNT was 171, TNB 151, RDX 167, and EDNA 160% of TNT (Ref 31)

Toluene. A mixt with toluene expld at the Kaiser Wilhelm Inst in 1917, and in 1920 at the Univ of Münster a massive iron gas burner containing a residue of 10g of a TenMe/toluene mixt decomposed suddenly. The deton splintered the container, and of 300 students in the area, 10 were killed and 20 injured (Ref 13b). A mixt with toluene which has an OB of zero is called “Pandastite” in Fr. It has a deton vel of 8000 m/sec (NG 7000m/sec) and is more shock sensitive than NG (Ref 31)

Refs: 1) Beil 1, 80, (21), (47), (116) & (107) 2) L. Schischkoff, Ann 119, 246 (1861) 3) A. Oustach, Ber 39, 2479 (1906) 4) A. Pictet & E. Khotinsky, Ber 40, 1136 (1907) 5) F.D. Chattaway, JCS 97, 2099 (1910) 6) I. Ostrov-isslenskii, JPraktChem (2) 84, 489 (1911) & CA 6, 1287 (1912) 7) A.K. Macbeth, Ber 46,

**METHANE, NITROSO.** CH₃NO; mw 45.04, N 31.10%, OB to CO₂ —88.81%. It is a blue gas at room temp, its solns in hydrophobic solvs are blue, in w and hydrophilic solvs are colorl (Ref 2); CA Registry No 865-40-7

**Preparation.** It was first prepd by the irradiation of tert-butyl nitrite with a Hg-vapor lamp and isolated as a colorl dimer which, when heated above its mp of 122.0—2.2°, is converted to the blue monomer; prolonged heating of the dimer converts it to the insoluble trimer of formaldehyde oxime (Ref 2). It has also been prepd in varying yield by the irradiation of compds capable of producing Me radicals, such as dimethyl mercury (Ref 5), tert-butyl peroxyde (Ref 8), azomethane, or Me iodide (Ref 10) in the presence of nitric oxide

**Reactions.** Monomeric nitrosomethane is condensed out at liq N temp to a pale blue solid which converts to the colorl dimer upon warming to room temp (Ref 6 & 7), and to formaldehyde oxime at higher temps (Ref 7). The structure proposed for the dimer is CH₃N:NCH₃

\[ \text{CH}_3\text{N:NCH}_3 \]

which can exist in cis- and trans-forms (Ref 6). The low yield of nitrosomethane in irradiation exps has been explained by its reactn with excess nitric oxide to form N dioxide, N, and polymeric prods (Ref 9)

**Spectroscopic Data.** Freshly prepd nitrosomethane has an IR absorption band at 6.3—6.4μ which slowly decays and is replaced by a band at 11μ characteristic of formaldehyde oxime (Ref 8). The visible absorption λₓmax is 287μm in eth and at 266—7μm in w (Ref 4)

Refs: 1) Beil, 1, (105) & (99) 2) C.S. Coe
& T.F. Doumani, JACS 70, 1516 (1948)
3) J.R. Raley et al, JACS 70, 88 (1948)
4) H.T.J. Chilton & B.G. Gownlock, JCS 1954, 3174
6) B.G. Gownlock & J. Trotman, JCS 1955, 4190
7) L. Batt & B.G. Gownlock, TrFaradSoc 56, 682
8) J.G. Calvert et al, JACS 82, 1
9) M.I. Christie et al, JCS 1964, 3147
10) M.I. Christie et al, TrFaradSoc 61, 674 (1965)

Nitroso Halogen Derivatives of Methane

**Difluoronitrosomethane**, F₃CHNO, mw 81.03, N 17.29%; prep'd by the photolysis of a mixt of chlorofluoromethane & nitric oxide


**Trifluorornitrosomethane**. F₃CNO; mw 99.01, N 14.15%; a deep blue solid, liq., or gas. The color of the liq. is described as that of a coned ammoniacal Cu sohn (Ref 2). The odor is described as earthy or similar to sewage sludge (Ref 2). Mp -196.6°, bp -84° (Refs 1 & 2); CA Registry No. 334-99-6

**Preparation**. It was first isolated as a by-prod from the fluorination of Ag cyanide. Its formation was attributed to the presence of Ag nitrate or Ag oxide in the tech grade Ag cyanide used (Ref 2). The first prepn in good yield was by the irradiation in a sealed tube of a mixt of nitric oxide and trifluoromethyl iodide plus a small amt of Hg with the light from a Hg vapor lamp, yield 75% (Ref 3).

The same workers also prep'd trifluorornitrosomethane by the reaction of Ag trifluoroacetate with nitrosyl chloride (CINO), yield 13% (Ref 5). More recent work indicated that this reaction proceeds thru the intermediate formation of the mixed anhydride of nitrous and trifluoroacetic acids (F₃CCONO) (Ref 11).

Another prepn reported is by heating trifluoroacetohydroxamic acid (F₃CCONHOH) to 85° at 30-40mm of Hg, yield 63% (Ref 10).

**Chemical Reactions**. It is readily oxidized with hydrogen peroxide to the nitro compd (Ref 4). It is stable in the absence of light or air for 3-5 years; but sunlight or irradiation with UV light converts it to o-nitroso-N,N-bis(trifluoromethyl)-hydroxylamine, (F₃C)₂NO(NO) (Ref 8). It reacts with perfluoroethylene to give a mixt of perfluoro-2-methyl-1,2-ozazetidine and a linear copolymer (Ref 6). This polymer, whose structure was shown to be (CF₂CF₂NO)ₙ, has been found to be an elastomer with very good chem resistance and low temp props. For a review of this type of elastomer see Ref 11. *Heat of Vaporization*. 4133cal/g, Trouton const 21.9 (Ref 7).

**Spectra. Infra Red.** The IR spectrum of a highly purified sample in the gas phase with assignment of bands is given in Ref 7.

**Visible.** The intense blue color of the compd is due to a broad absorbtion band at 6800-40Å, εₘₐₓ = 19.0 (Ref 4). This band is present in the gas phase and in solns (Ref 9).

**Toxicity.** Its inhalation causes headaches and an unwell feeling (Ref 2)


**Chloronitrosomethane.** See Chloromethane and Derivatives in this Vol.

**Chlorodifluoronitrosomethane.** CICF₂NO, mw 115.47; N 8.24%; a dark blue liq. or gas; bp ca -35° (Refs 1, 2, & 6); CA Registry No. 421-13-6

**Preparation.** It has been prep'd by reactions analogous to those for prepn of trifluoronitrosomethane (Refs 2 & 5). It has also been prep'd by the action of 33% aq nitric acid on chlorodifluorosulfenyl chloride (CICF₂SCI) (Ref 3), and by the action of hot concd HCl on difluoronitroacetic acid (Ref 4). Its props and reactions are similar to trifluoronitrosomethane


**Dichlorofluorooritoxosmethane.** FCCl2NO, mw 131.93, N 10.61%; a blue liq, bp 12°C (Ref 2); CA Registry No 1495-28-9. It is prepd by the action of 33% nitric acid on FCCl2SCI, yld 8% (Ref 2); and by the action of K chloride on fluorochloronitroacetic acid (Ref 3).

A soln of the compd in eth was treated overnight with hydrogen sulfide in a sealed tube to give FCIC: NOH which polymerized in a few days (Ref 2).


**Trichloronitrosomethane.** Cl3CNO, mw 148.39, N 9.51%, OB to CO2 -10.78%; a deep blue liq, comparable in color to ammoniacal Cu solns; freezes at liq N temp to a violet-blue solid; bp 57-58°C, d at 20°C, 1.500g/cc (Refs 1, 2 & 3); CA Registry No 37114-19-7

**Preparation.** It was first prepd by the action of 10% nitric acid on Na trichloromethanesulfonate (Cl3CSO2Na) (Ref 2). It has also been prepd by the reduction of chloropirin (Cl3CNO2) at a Pt cathode in 40%aq sulfuric acid contg et alc (Ref 4); by heating trichloroacetohydroxylic acid (Cl3CCONHOH) to 90°C and 20-30mm, yld 62% (Ref 5); and by the interaction of Na trichloromethanesulfonate and nitrosyl chloride in a sealed tube (Ref 7). Most interesting is the report that when nitric oxide was passed thru C tetrachloride while being irradiated with high-energy electrons, the soln turned dark blue, and a 50% yield of trichloronitrosomethane was obtd (Ref 6).

**Chemical Reactions.** It decompd slowly on standing, more rapidly on heating in the absence of air to form nitrosyl chloride, nitric oxide, chloropirin, & trichloromethylchloromethyl-eneimine (Cl3CN-CCl3) (Ref 2). It degradates in the presence of O2 at 120°C to give N dioxide, chloropirin, and hexachloroethane (Ref 2). It is reduced to Me amine with Fe turnings and acel ac (Ref 2); and to phosgene oxide (Cl2C: NOH) with hydrogen sulfide in Me alc (Ref 2), or Sn dichloride and HCl (Ref 3)

**Solubility.** It is insol in w, sol in org solvs (Ref 2)


**Bromodichlorofluorooritoxosmethane.** BrCCl2NO, mw 159.93, N 8.76%; it is a dark blue solid & liq; bp ca -12°C. It is prepd by the irradiation of a mixt of bromodifluorooiodomethane and nitric oxide in a sealed tube in the presence of Hg, yld 50%

**Refs:** 1) Beil 1, (100) 2) R.N. Hazeldine, JCS 1953, 2075

**Bromodichlorofluorooritoxosmethane.** BrCCl2NO, mw 192.84, N 7.26%; it is a dark blue liq of unpleasant odor, frp -80°C, bp 21°C at 24mm. It is prepd by the action of Br and Na acetat on phosgene oxide (Cl2C: NOH). It decompd on attempted distn at atm press. It is reduced to phosgene oxide with hydrogen sulfide in Me alc, and warming with Br produces dichlorodibromomethane

**Refs:** 1) Beil 1, (105) 2) L. Birkenbach & K. Sennewald, Ber 65, 546 (1932)

**Chlorodibromonitrosomethane.** CICBr2NO, mw 237.31, N 5.90%; it is a dark blue liq of unpleasant odor, it freezes at -80°C, bp 24°C at 20mm; it can only be distd in a vacuum. It is prepd by action of Br and Na acetae in w on bromochloroformoxime (BrCOCI: NOH). Heating with Br forms chlorotribromomethane

**Refs:** 1) Beil 1, (105) 2) L. Birkenbach & K. Sennewald, Ber 65, 546 (1932)

**Tribromonitrosomethane.** Br3CNO, mw 281.77, N 4.97%; it is a dark blue liq of unpleasant odor; bp 36-38°C at 14mm, decomp above 50°C. It is prepd by the action of K hypobromite on MF (Ref 2), or by the action of KBr and Na acetae on MF (Ref 3). Upon warming with w forms tetrabromomethane and cyanogen bromide (Ref 3)

**Refs:** 1) Beil 1, (106) 2) G. Endres & H. Bottmann, Ber 65, 67 (1932) 3) L. Birkenbach & K. Sennewald, Ber 65, 546 (1932)

**Written by:** C. H. McDonnell
**Methanites.** Safety expls used in coal mining. Pelant (Ref.) details eight compn variations, of which Methanites VII and VIII proved to be the safest. They were gallery tested in methane-air-coal dust atms in 200 to 500g charges, and produced about 1.8% ignitions. In actual use in gaseous and dusty coal mines, no ignitions or explns occurred. The formulations for the eight Methanites, results of output tests, calc'd expl temps, and results of gallery tests are given below:

<table>
<thead>
<tr>
<th>Formulation, %</th>
<th>Methanites</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroglycerin</td>
<td></td>
<td>28.60</td>
<td>28.40</td>
<td>26.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td></td>
<td>1.05</td>
<td>1.04</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.8</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Centralite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid DNT</td>
<td></td>
<td>0.70</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood flour</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerin</td>
<td></td>
<td>2.20</td>
<td>2.17</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dextrin</td>
<td></td>
<td>2.20</td>
<td>2.17</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca nitrate in 50% soln</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Amm nitrate</td>
<td></td>
<td>27.75</td>
<td>27.53</td>
<td>29.4</td>
<td>32.0</td>
<td>23.0</td>
<td>23.1</td>
<td>23.25</td>
<td>25.0</td>
</tr>
<tr>
<td>Na chloride</td>
<td></td>
<td>31.10</td>
<td>36.80</td>
<td>38.5</td>
<td>40.0</td>
<td>46.5</td>
<td>46.65</td>
<td>46.65</td>
<td>45.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td>0.40</td>
<td>0.40</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td>0.80</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palatino A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Output Tests**

<table>
<thead>
<tr>
<th>Test</th>
<th>Methanites</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trauzl test, cc.⁸</td>
<td></td>
<td>240</td>
<td>230</td>
<td>225</td>
<td>190</td>
<td>170</td>
<td>170</td>
<td>165</td>
<td>170</td>
</tr>
<tr>
<td>Kast test, mm ⁹</td>
<td></td>
<td>0.91</td>
<td>0.86</td>
<td>0.85</td>
<td>0.82</td>
<td>0.68</td>
<td>0.67</td>
<td>0.50</td>
<td>0.66</td>
</tr>
<tr>
<td>Gap test, cm ⁷</td>
<td></td>
<td>5–6</td>
<td>4–5</td>
<td>2–4</td>
<td>2</td>
<td>2</td>
<td>1–2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Expln Temp (calcd), °C, by method of:**

- Berthelot & Vieille: 2176 2103 2002 1778 1631 1576 1555 1633
- Pier & Bjerrum: 3294 3229 3048 2707 2513 2431 2380 2504

**Gallery Test**

<table>
<thead>
<tr>
<th>Methanites</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.7</td>
<td>21.2</td>
<td>19.8</td>
<td>11.6</td>
<td>5.5</td>
<td>4.2</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

---

⁸ Trauzl Pb block test, 10g sample, No 6 cap
⁹ Kast's crusher test, 10g sample, Cu cylinder
⁷ Transmission of detonation

*Ref:* V. Pelant, *Chem&Ind* (Paris), Special No (June 1933), 888–901
Methanol (Methyl alcohol, wood alcohol). CH₃OH, m.w 32.04; OB to CO₂ = 149.81%; clear, colorless, mobile, highly polar liquid; mp -97.8°, bp 64.5°, d 0.7913g/cc at 20/4°, flash p 54°F, autoign temp 86°F, vapor press 100mm at 21.2°C; miscible with water, alcohol & ether. Can be prepared by the high pressure catalytic synthesis from carbon monoxide and hydrogen, or by partial oxidation of natural gas hydrocarbons. Other methods of preparation and properties are given in Ref 1. It is used in the manufacture of formaldehyde and dimethyl terephthalate, chemical synthesis (methyl amines, methyl chloride, methyl methacrylate, etc), aviation and rocket fuel (Ref 3), automotive antifreeze, solv for NC, ethyl cellulose, polystyrene butyral, shellac, resin, manila resin, dyes; denaturant for alcohol; dehydrator for natural gas (Ref 4). Nobel used methanol as an additive to gasoline to reduce its sensitivity for transportation purposes. In this case it was removed by water wash prior to use (Ref 2). Methanol can be nitrated directly to form methyl nitrate (see in this Vol), a powerful explosive compound.

Methanol is a dangerous fire hazard when exposed to heat or flame, and a moderate explosion hazard when exposed to flame. It is a dangerous disaster hazard upon exposure to heat or flame, and it can react vigorously with oxidizing materials. Methanol possesses distinct narcotic properties, and it is also a slight irritant to the mucous membranes. Its main toxic effect is exerted upon the nervous system, particularly the optic nerves and possibly the retina. In the body the products formed by its oxidation are formaldehyde and formic acid, both of which are toxic. Because of the slowness with which it is eliminated, methanol should be regarded as a cumulative poison (Ref 5).

Methanol is available in technical, C.P. (99.85% purity) and electronic (used to cleanse and dry components) grades. US Spec 0-M-232E (July 30, 1968) with Amd 1 (Sept 11, 1970), covers the requirements and tests for methanol used by all Federal agencies (see below).


METHANOL, Analytical Procedures

1.1 Scope. This Spec and Amd 1 covers methanol of synthetic grades and a denaturing grade.

1.2 Classification. Methanol shall be of the following grades:

Grade A — Synthetic, 99.85% by wt (solvent use)
Grade AA — Synthetic, 99.85% by wt (hydrogen—carbon dioxide generation use)
Grade C — Wood alcohol (denaturing grade)

2.1 Applicable Documents — Listed among them are:

b) Military Specification MIL-G-10157, "Generator and Charging Plant, Hydrogen and Carbon Dioxide, Semitrailer-Mounted".
c) Military Standard MIL-STD-147 "Palletized and Containerized Unit Loads 40" x 48" 4-Way (Partial) Pallet Skids, Runners, or Pallet-Type Base".
d) Military Standard MIL-STD-290, "Packaging, Packing, and Marking of Petroleum and Related Products", Publications b, c and d, required by contractors in connection with specific procurement functions, should be obtained from the procuring activity or as directed by the contracting officer.

3. Requirements.

3.1 Grades A and AA. Shall conform to Table 1

3.2 Grade C. Grade C wood alcohol (denaturing grade) shall comply with Internal Revenue Service Regulations SDAI of 26-CFR-212, “Formulas for Denatured Alcohols”

4. Quality Assurance Provisions, which include:

4.1 Responsibility for Inspection

4.1.1 Material Inspection

4.2 Classification of Inspection

4.3 Quality Conformance Inspection

4.3.1 Lot

4.3.2 Drums and Small Containers

4.3.3 Tank Cars

4.3.4 Lot Acceptance

are discussed on p 3 of Spec 0-M-232E

4.4 Quality Conformance Inspection.

4.4.1 Chemical Reagents. Wherever chemical reagents are specified in the following tests, analytical reagent grade shall be used

4.4.2 Acetone and Aldehydes. Determine the acetone and ethanol content in accordance with ASTM D1612. The sample is reacted with Nessler’s reag and the turbidity that is produced is compared to a standard contg the equivalent of 0.003 weight % acet

4.4.3 Acetone and Ethanol (Grade AA only). Determine the acetone and ethanol content by the elution method of gas chromatography using internal standards

4.4.3.1 Apparatus and Operating Conditions. A conventional chromatographic technique utilizing an instrument at least equal in performance to the highest sensitivity range of the Perkin Elmer Vapor Phase Fractometer Model 154 shall be used. A two meter elution column

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Grade A Requirement</th>
<th>Grade AA Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone and aldehydes, % max</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Acetone, % max</td>
<td>—</td>
<td>0.001</td>
</tr>
<tr>
<td>Ethanol, % max</td>
<td>—</td>
<td>0.001</td>
</tr>
<tr>
<td>Acidity (as Acetic Acid), % max</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Alkalinity, % max as NH₃</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear and free from suspended matter or sediment</td>
<td>No discoloration</td>
</tr>
<tr>
<td>Carbonizable substances</td>
<td>Not darker than color standard No 5 of ASTM platinum-cobalt scale</td>
<td>No discoloration</td>
</tr>
<tr>
<td>Color</td>
<td>Not more than 1° and shall include 64.6° ± 0.10° at 760mm</td>
<td></td>
</tr>
<tr>
<td>Distillation range</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>No cloudiness or opalescence</td>
<td>No cloudiness or opalescence</td>
</tr>
<tr>
<td>Specific gravity, max</td>
<td>0.7928 at 20°/20°</td>
<td>0.7928 at 20°/20°</td>
</tr>
<tr>
<td>% Methanol by weight, min</td>
<td>99.85</td>
<td>99.85</td>
</tr>
<tr>
<td>Nonvolatile content, g/100ml, max</td>
<td>0.0010</td>
<td>0.0010</td>
</tr>
<tr>
<td>Odor</td>
<td>Characteristic, nonresidual</td>
<td>Characteristic, nonresidual</td>
</tr>
<tr>
<td>Permanganate test</td>
<td>No discharge of color in 30 minutes</td>
<td>No discharge of color in 30 minutes</td>
</tr>
<tr>
<td>Water, % max</td>
<td>0.15</td>
<td>0.10</td>
</tr>
</tbody>
</table>
using tetraethylene glycol dimethyl ether (TEDME) or equal as the liquid phase shall be used under the following operating conditions: temp, +55°C; press, adjust to produce He flow rate of 80 ± 10ml; sample size, 0.20ml

4.4.3.2 Quantitative Analysis.

(a) Internal standards for quant analysis curves shall be run on standard specimens prep'd by adding pure ethanol or acet in 0.001% by vol increments. The area under the peak is equal to the concn of ethanol or acet in the specimen. Using a simple ratio, the concn of ethanol or acet can be calc'd

(b) The area under the ethanol or acet curve of the unknown sample, when calc'd utilizing the internal standardization method, shall be no more than specified in Table 1

4.4.4 Acidity. Determine the acidity in accordance with ASTM D1613. The sample is mixed with an equal vol of w and titrated with aq NaOH soln to the phenolphthalein end point

4.4.5 Alkalinity. To 25ml of w, add 1 drop of 0.1% methyl red indicator soln (60% alc) and 0.01N acid or base until the soln is just pink. Add 25ml of specimen, mix well, then titrate with 0.01N sulfuric acid until the pink color is restored. Calc the % NH₃ by wt as follows:

\[ \% \text{alkalinity as NH}_3 = \frac{(\text{ml of H}_2\text{SO}_4)(\text{Normality of H}_2\text{SO}_4)(1.703)}{(\text{ml of specimen})(0.79)} \]

4.4.6 Appearance. The specimen shall be thoroughly mixed and shall be examined by transmitted light for clarity, suspended matter, or sediment. This is most readily done by pouring some of the specimen into a test tube or Nessler tube

4.4.7 Carbonizable Substances. Pipette 5ml of the sample into a 20x150mm test tube. Slowly and carefully add 5ml of concd H₂SO₄ and swirl the tube gently during the addition. The H₂SO₄ used must be no darker in color than the methanol. Do Not Cool The Mixt. Allow the tube and contents to stand for 5 minutes at room temp. Examine the contents visually for any evidence of discoloration

4.4.8 Color. Det color in accordance with ASTM D1209. The sample is compared spectrophotometrically against platinum-cobalt standard solns

4.4.9 Distillation Range. Det the distn range in accordance with ASTM D1078, with the following exceptions: (a) measure the 100ml of specimen and distillate at room temp (without w bath); (b) det temp using JL-4 type thermometer having a range of 45° to 70° in increments of 0.1°. In this method a 100ml sample is distd under conditions equiv to a simple batch differential distn. The temp of the Hg in the thermometer is equilibrated with that of the refluxing liq before the distillate is taken over. Boiling temps observed on a partial immersion thermometer are corrected to std atmos press to give true boiling temps

4.4.10 Hydrocarbons. Dil 15ml of the specimen to 45ml with distd w in a Nessler tube. Visually examine for cloudiness or opalescence during 30 minutes of standing

4.4.11 Specific Gravity (Methanol Content). Det the sp gr with a pycnometer of about 50ml capacity or by any other method accurate to the fourth decimal place. In the temp range 15 to 25°, the sp gr changes 0.00094 per degree. This correction factor shall be multiplied by the number of °C difference between 20° and the temp of the specimen. This resulting number shall be added to the detd sp gr of the specimen when the temp is greater than 20° and subtracted when the temp is lower than 20°. Det the methanol content from the sp gr based on the following:

<table>
<thead>
<tr>
<th>% by Weight</th>
<th>Specific Gravity at 20/20°</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.7</td>
<td>0.79330</td>
</tr>
<tr>
<td>99.8</td>
<td>0.79298</td>
</tr>
<tr>
<td>99.85</td>
<td>0.79283</td>
</tr>
<tr>
<td>99.9</td>
<td>0.79267</td>
</tr>
<tr>
<td>100.0</td>
<td>0.79236</td>
</tr>
</tbody>
</table>

4.4.12 Nonvolatile Content. Det nonvolatile content in accordance with ASTM D1353, except that specimen shall be 500ml (see Vol 6, p E158-L)

4.4.13 Odor. Det odor in accordance with ASTM D1296. In this test strips of filter paper are dipped into specimen and reference standards, and odor comparisons are made of "characteristic" odor when the strips are wet, and "residual" odor remaining after the strips appear dry. If an odor persists on the sample paper after the point in time when no odor is detectable on the standard paper, the odor is reported as "residual"
4.4.14 Permanganate Test. Det permanganate
time in accordance with ASTM D1363. Sub-
stances reacting with K permanganate in neutral
soils reduce it to Mn dioxide which colors the
soil yellow. In this test the time required for
the color of the test soil to change to that of
a standard soil is measured. The color of the
test soil changes from pink-orange to yellow-
orange

4.4.15 Water Content. Det w content in ac-
\textit{cording} with ASTM D1364 (see Vol 6, p
E158-R)

\textbf{METHAZONIC ACID AND ITS SALTS}

\textbf{Methazonic Acid (Nitroacetaldoxime).}
C\textsubscript{2}H\textsubscript{4}N\textsubscript{2}O\textsubscript{3}, mw 104.07, N 26.92%, OB to CO\textsubscript{2}
\(-46.12%\); leaflets from eth,
\begin{align*}
\text{CH}_2\text{NO}_2 & \quad \text{prisms from benz and plates}
\text{CH3}=\text{NOH} & \quad \text{from chlf; mp 79° (de}-
\text{CH3}=\text{NOOH} & \quad \text{compn), bp (explds at}
\text{CH3}=\text{NOH} & \quad \text{150°); sol in w, alc, eth,}
\text{CH3}=\text{NOH} & \quad \text{acet, warm benz and chlf.}
\text{NO} & \quad \text{Can be prep by heating}
\text{Cl} & \quad \text{nitromethane with alc}
\text{CN} & \quad \text{NaOH or by treating nitro}-
\text{N} & \quad \text{methylene with aq ammonia}
\text{O} & \quad \text{at a temp below 10° (Refs 2, 3 & 4)}
\end{align*}

Methazonic acid is an expl, less powerful than
TNT (Trauzl block expansion 240cc vs 290cc
for TNT) but more sensitive to impact (com-
parable to PA). It is unstable in storage

Methazonic acid forms numerous salts, some
of which are expl (Ref 1). The salts were prep-
either by treating the acid with carbonates or
oxides of the corresponding metals, or from Na
or K methazonates by double decom-

\textbf{Ammonium Methazonate.} NH\textsubscript{4}C\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2}.
Cryst; sol in methanol, less in alc; nearly insol in
eth and chlf. Deflagrates on rapid heating

\textbf{Lead Methazonate.} Pb(C\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2})\textsubscript{2}. Cryst;
explds on impact or when heated to 220°

\textbf{Mercury Methazonates.} Forms two salts; mer-
curic, Hg(C\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2})\textsubscript{2} and mercurous,
Hg\textsubscript{2}C\textsubscript{2}H\textsubscript{2}O\textsubscript{3}N\textsubscript{2}. The former explds at 160°,
the latter at 170°. Both salts explde on impact

\textbf{Potassium Methazonate.} K\textsubscript{2}C\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2}. Needles;
explds violently when heated to 195°. Urbaniński
and Kowalczyk (Ref 5) considered it the best
expl of all the methazonates examined by them

\textbf{Silver Methazonate.} AgC\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2}. Yellowish
powd, darkening slowly by action of light.
Explds violently when heated to about 160°

\textbf{Sodium Methazonate.} NaC\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2}. Cryst;
explds mildly at 245°

\textbf{Thallium Methazonate.} TlC\textsubscript{2}H\textsubscript{3}O\textsubscript{3}N\textsubscript{2}. Cryst;
explds violently when heated to about 235°.
It was the most sensitive to impact (4cm with a
2kg weight) of all the methazonates (Ref 5).

\textbf{Refs:} 1) Beil 1, 627, (331) & [684] 2) P.
Fries, Ber 9, 394 (1876) 3) W.R. Dunstan &
E. Goulding, JCS 77, 1262 (1900) 4) W.
Steinkopf & C. Kirchoff, Be 42, 617–21 &
2026–31 (1909) & CA 3, 1155 & 2438 (1909)
5) T. Urbaniński & M. Kowalczyk, SS 32, 42
(1937) (This is an abstract of a paper in the
Polish journal, Wiadomosci Techniczne Uzbro-
jenia 4, 22–34 (1935)

\textbf{Methilites.} Liq expls developed in the USA
during WWII for use in linear charges for mine
field clearance. Typical of these were:

\textbf{Methilite 20:} NG/EDGN 75/25 80, DMePh 20
& EtCent 0.8% (added)

\textbf{Methilite 25:} NG/EDGN 75/25 75, DMePh 25
& EtCent 0.75% (added)

\textbf{EL-389A:} NG/EDGN 75/25 55, DNT oil/TNT
70/30 45 & DPhA 0.55% (added)

\textbf{EL-389B:} NG/EDGN 75/25 60, DNT oil/TNT
70/30 40 & DPhA 0.6% (added)

Storage stability problems were encountered
with all of these exps
Ref: L.H. Eriksen, "Properties of Liquid Exp-
losives", PATR 1542 (2 July 1945)

\textbf{METHOXY NAPHTHALENES
AND DERIVATIVES}

\textbf{Methoxynaphthalenes.} C\textsubscript{14}H\textsubscript{11}O\textsubscript{2}. mw
158.21. There are two isomers: 1-methoxy- &
2-methoxy naphthalene

\textbf{1-Methoxy-Naphthalene (Methyl-\alpha-naphthyl-
ether)}
\begin{align*}
7 & \quad 1-O-CH\textsubscript{3}, liq, mp \sim 10^\circ,bp 269^\circ,
8 & \quad d 1.0964g/cc at 14/2^\circ, RI
6 & \quad 1.6940 at 25^\circ; sol in alc,
5 & \quad eth & benz. Prepn from
4 & \quad K-\alpha-naphthalate by heating with methylchloride
3 & \quad at 280^\circ
\end{align*}
Ref: Beil 6, 606, (306), [578] & (2922)
2-Methoxy-Naphthalene (Methyl-β-naphthyl-ether). Cryst, mp 73–74°, bp 274°. Sol in eth, chlf & benz. Prepn from Kβ-naphthalate by heating with methyl chloride at 300°
Ref: Beil 6, 640, (312), [615] & [2926, 2969]

2,4-Dinitro-5-Methoxy-1-Acetoxy-Naphthalene
(3-Acetic acid-(2,4-dinitro-5-methoxy-naphthyl-1)-ester), [2,4-Dinitro-5-methoxy-naphthyl-1] acetate). (O2)N2C10H4(C2H3O2)O.CH3, mw 306.25, N 9.15%, OB to CO2 –125.39%, gold cryst, mp 154° (decomp). Prepn from 2,4-dinitro-5-methoxy-naphthol by refluxing with ACO & concd sulfuric acid
Ref: Beil 6, [5274]

4,6-Dinitro-5-Hydroxy-1-Methoxy-Naphthalene
(2,8-Dinitro-5-methoxy-naphthol-1), methyl-[4,6-dinitro-5-hydroxy-naphthyl-1]-ether). (O2)N2C10H4(OH).O.CH3, mw 278.24, N 10.07%, OB to CO2 –132.26%, gold needles from alc, mp 183° (decomp). Sol in alc. Prepn from 5-methoxy-1-acetoxy-naphthalene by reaction with an excess of nitric acid (d 1.42 g/cc) at 0°
Ref: Beil 6, [5274]

5,7-Dinitro-8-Hydroxy-1-Methoxy-Naphthalene
(3-Methyl-[5,7-dinitro-8-hydroxy-naphthyl-1]-ether, 2,4-Dinitro-8-methoxy-naphthol-1). (O2)N2C10H4(OH).O.CH3, mw 264.21, N 10.61%, OB to CO2 –121.12%, gold plates from alc, mp 179–80° (decomp). Sol in dil alkali & alc. Prepn from 2,4-dinitro-1,8-dimethoxy-naphthalene by reaction with 2N NaOH
Ref: Beil 6, [5284]

6,8-Dinitro-6-Hydroxy-1-Methoxy-Naphthalene
(2,4-Dinitro-6-methoxy-naphthol-1), methyl-[6,8-dinitro-6-hydroxy-naphthyl-1]-ether). (O2)N2C10H4(OH).O.CH3, mw 264.21, N 10.61%, OB to CO2 –121.12%, orange needles from CCl4, mp 173° (decomp). Sol in CCl4. Prepn from 2,4-dinitro-naphthlenediol-1,5 by reacting with an excess of dimethyl sulfate in dil NaOH
Ref: Beil 6, [5273]

2-Methoxy-1-Chloromethyl-Naphthalene
(Methyl-[1-chloromethyl-naphthyl-2]-ether). (ClCH2)C10H6.O.CH3, mw 206.78, OB to CO2 –220.52%, cryst from pet ether plus benz or from alc, mp 120–23° (decomp). Sol in alc & pet ether plus benz. Prepn from an AcOH soln of 2-methoxy-naphthalene reacted with a HCl satd suspension of paraformaldehyde in AcOH
Ref: Beil 6, [3020]

Methyl Abietate (Methyl resinate or Methyl sylvate). (The commercial product, contg about 90% of MeAb, manufd by the Hercules Powder Co, is named “Abalyn”). C19H29COOCH3, mw 316.47, color to faintly amber liq with pleasant, ester-like, odor; mp, does not freeze, even at –40°, but becomes very viscous; bp 360–65° (with sl decomp), d 1.040g/cc at 20° (1.020–1.030 for Abalyn); RI 1.5295 at 20°, flash p 180° and fire p 218° (Cleveland open cup); viscosity 28–30 poises at 25°; saponification No 20–25; acid No 6 or less; sp ht 0.395 between 25–27°. Can be obtained commercially by esterification of either abietic acid, or of resin with methanol at high temps. In the lab, it is possible to prepare it by heating an alkali resinate with a methyl halide. It is miscible with most org solvents. Has been proposed as a plasticizing resin for lacquers, including those of NC, and as a coating for some progressive burning proplnts. It is v sl volatile (5.6mm Hg at 200°, compared with 22.4mm Hg for dibutyil phthalate), and possesses very satisfactory thermal stability, being stable up to 350°. It is practically noncorrosive and does not develop acid on hydrolysis

Being an unsatd compd with one double bond, it is markedly subject to oxidn, and when left in air, dries and turns yellow. As this property reduces its usefulness in some applications, methods were developed whereby the reactive double bond was satd with H2. The resulting compd is:

Methyl Dihydroabietate (Commercial product developed by Hercules Powder Co under name “Hercelyn”. Another product is “Hercelyn-D”, which is Hercelyn deodorized by steam-blowing). C19H31COOCH3, mw 318.48, color to faintly amber colored liq; mp, does not freeze at –40°, but becomes very viscous; bp 356–70° with sl decomp; d 1.020–1.030g/cc for Hercelyn; flash p 183° and fire p 218° (Cleveland open
cup; RI 1.517 to 1.519 at 20°C, viscosity 28–34 poises at 20°C; acid No 6 or less; saponification No 20–25

Can be prepd by catalytic hydrogenation of methyl abietate. "Hercolyn" possesses excellent thermal stability. It does not corrode metals and does not develop acid on hydrolysis. Its volatility is very low (4.5 mm Hg at 200°C).

Both "Hercolyn" and "Abalyn" combine the solvent power of abietic acid with that of a methyl ester. Thus, they may act as resins and as plasticizers. Both possess excellent wetting ability, even for nonporous materials such as glass and metals. Hercolyn was proposed (Refs 2 & 3) as a coating for NC proplnt grains. Refs: 1) Beil — does not list abietic acid (abi-
etinsäure) or "methyl-abietaete" 2) E.S. Good-

**Methyl Acetate** (Essigäuremethylster in Ger), CH₃COOCH₃, mw 74.08, OB to CO₂ —151.19%, colorless, vol liq, mp —98.05°C, bp 54.05°C, flash p 15°F, d 0.9249/g/cc, RI 1.3619 at 20°C, autoign temp 935°F. Can be prepd by heating methanol with acet ac in the presence of sulfuric acid. Sol in w, miscible with alc, eth and com-
mon hydrocarbon solvents.

Good solv and plasticizer for cellulose esters, including NC's, except for those with very high N contents. Refs: 1) Beil 2, 124, (52) & [125] 2) CondChemDict (1971), 563-L

**Methyl Acetoacetate** (Acetessigäuremethylster in Ger), CH₃COCH₂COOCH₃, mw 116.11, OB to CO₂ —151.58%, colorless, liq, mp —80°C, bp 171.7°F, d 1.0785/g/cc at 20/20°C, flash p 158°F, vap press 0.7 mm at 20°C. Can be prepd by treating methylacetate with metallic Na and

decomp the resulting Na compd with acet ac. SI sol in w (38p at RT), sol in alc, eth and et acet. Used as a solv for cellulose ethers or as an ingred of solv mixts for cellulose esters. Refs: 1) Beil 3, 632, (223) & [414] 2) CondChemDict (1971), 563-L

**Methyl Acetone.** Commercial product; a water-
white, anhyd lrq, consisting of various mixts of acet (45 to 65%), methyl acetate (20 to 30%) and methanol (20 to 40%). Density about 0.83g/cc, boiling range 50 to 70°C, flash p near 0°F. Miscible with hydrocarbons, oils and w.

Obtained as a by-product in the manuf of acet and methanol from wood distn, representing fractions which cannot be economically sep. The mixt can be used as such, being an excellent solv and plasticizer for NC and other cellulose esters, such as the acetate. It also dissolves rubber, gums, resins, lacquers, paint and varnish. Refs: 1) T.H. Durrans, "Solvents", Van-

**Methyl Alcohol.** See Methanol

**Methylacetylene (Allylene, Propyne).** CH₃C≡CH, mw 40.07, colorless liquifed gas; bp —23.1°C, fr p —101.5°C; flammable, dangerous fire and expl risk. It is self-reactive, and can decomp explosively at 4.5 to 5.6 atms press (Ref 2).

An expln occurred at Dow's Freeport, Texas plant in 1960 while workers were loading a small tank of methyl acetylene. Following this expln, a 2000 gal tank blew up and burned for 1½ hours. The cause of the blasts were not detd (Ref 1).


**Methylaluminum Diazide.** CH₃Al(N₂)₃, mw 126.08, N 66.67%, white powd. When a frozen eth soln of Al(CH₃)₃ and excess HN₃ is thawed, reaction begins at room temp with evolution of CH₄ and pptn of a fine white powd, methyl-
aluminum diazide. The reaction is completed
in two hours. It is sol in tetrahydrofuran; evolves CH4 on addition of HCl; is oxidized to CH4OAl(N3)2 on exposure to air; effloresces in moist air; is not sensitive to percussion; sputters in a flame with white light and emission of Al oxide snow; decomposes in excess w with evolution of methane; reacts with dil sulfuric acid with bright fire and occasional exp, and reduces Ag nitrate to metallic Ag in tetrahydrofuran soln Refs: 1) Bel’- not found 2) E. Wiberg & H. Michaud, Z Naturforsch 9b, 497 (1954) & CA 49, 767 (1955)

METHYLAMINE AND DERIVATIVES

Methyamine. This article supplements the one in Vol 1, A225-7 under Aminomethane and Derivatives; CA Registry No 74-89-5

Uses in Explosives. Gaseous methyamine is passed into solid Amm Perchlorate below -6.3° to give useful monopropellants. A mixt so prepped of 85% Amm Perchlorate and 15% methyamine has an Isp of 230 lbs/sec/lb at 20atm (Ref 1). A paste of 90.36 AN, 7.78% methyamine, and 1.85% inert is a blasting exp (Ref 2). Mixts of AN with 6-9% methyamine are blasting exps, and with 15-40% are propellants. A mixt of 65.5% AN, 14.5% methyamine and 20% unsymmetrical dimethylehydrazine has an Isp of 161 lbs/sec/lb and gives 25.4cuft of gas/sec at 174°F. Similarly a mixt of 65.5% AN, 28.5% methyamine, and 5% hydrazine gives 23cuft of gas/sec; and a mixt of 72.1% AN and 27.9% methyamine gives an Isp of 181 lbs/sec/lb at 300 lbs press (Ref 3)


Methyamine 5-Aminotetrazole Salt, CH3NH2.CH3N3, C2H8.N6, mw 116.13, N 72.37%. It is prepd by the interaction of the components in the min quant of hot ethyl alc, softens at 95°; mp 112–17°. Its exp props are unknown

Refs: 1) Bell – not found 2) R.A. Henry, JACS 74, 6303 (1952)

Methyamine Azide, CH3NH3.N3, CH3N4, mw 74.09, N 75.63%. It is prepd by heating MeNHCON3 with w (Ref 2), or by the action of hydrazoic acid on aq methylamine (Ref 3). It is obtd as delg crys which do not melt. It is slightly sol in w and ethyl alc; insol in eth (Ref 3). Its expl props are unknown

Refs: 1) Beil 4, [318] & [90] 2) E. Oliveri- Mandala, Gazz 43, 1, 538 (1913) & CA 7, 3755 (1913) 3) A. Cirulis & M. Straumanis, JPraktChem 161, 65 (1942) & CA 37, 5022 (1943)

Methyamine Complex with Cupric Azide, (MeNH2)2Cu(N3)2, C2H16CuN8, mw 209.74, N 53.40%. It is prepd by the interaction of the components, mp 126–28° (Ref 2). It is insol in inert solvs, decomp in hot w, explds at 180–90°, and is not shock sens (Ref 2).

Refs: 1) Beil 4, [91] 2) M. Straumanis & A. Cirulis, ZAnorgChem 251, 341 (1943) & CA 37, 6574 (1943)

Methyamine Cupric Bromate Complex, (MeNH2)2Cu(BrO3)2, C4H2OBr2CuN4O6, mw 443.64, N 12.63%. It is prepd by the interaction of methyamine and Cu(II)bromate and is obtd as blue crys which expld in 30secs at 86°


Methyamine Cupric Chlorate Complex, (MeNH2)2Cu(ClO4)2, C4H2OCl2CuN4O6, mw 354.61, N 15.80%. It is prepd by satg an aq soln of Cu(II)chlorate with methyamine and is obtd as dark blue crys which are hydrolyzed in w. When heated in a glass tube at 4°/min, it explds at 122°

Refs: 1) Beil 4, [91] 2) J. Amiel, CR 199, 51 (1934) & CA 28, 5361 (1934)

Methyamine Cupric Perchlorate Complex, (MeNH2)2Cu(ClO4)2, C4H2OCl2CuN4O8, mw 386.72, N 14.49%. It is prepd by the interaction of methyamine and Cu(II)perchlorate and is obtd as blue crys which expld in 30secs at 247°


by the addn of an ethyl alc soln of the acid to the amine in ethyl alc; mp 157.5°. It is a solid deriv useful for the identification of methylamine

Methylamine Salt of Ethyl Nitroacetate, 
MeNH₂·O₂NCH₂COEt, C₅H₁₂N₂O₄, mw 164.16, N 17.07%, OB to CO₂ –78.0%. Prepd by the interaction of its components; mp 110–115°
Refs: 1) Beil — not found 2) M. Kocôr et al, RočekChem 31, 1037 (1957) & CA 52, 8281f (1958)

Methylamine MEDINA Salt, 
2MeNH₂·(O₂NHNH₂)CH₂, mw 198.19, N 42.14%, OB to CO₂ –72.7%. It is prepd by the action of methylamine on MEDINA in ethyl alc and is obtd as hygr crysts, mp 120° with decmpn
Refs: 1) Beil 4, (93) 2) F. Chapman et al, JCS 1949, 1641

Methylamine Hydrobromide Cupric Azide Complex, (MeNH₂+)BrCu(N₃)₂–Br–, CH₄BrCuN₄, mw 259.61, N 37.77%. Dark violet crysts, mp 116°. It detonates with a hammer blow
Refs: 1) Beil 4, (91) 2) M. Straumanis & A. Cirulis, ZAnalChem 252, 9 (1943) & CA 38, 3563 (1944)

Methylamine Nitrate, bp 230° with yellowing (Ref 2), Q₁ 218.4kcal/mole (Ref 1), max d obtainable under press of 500kg/sqin is 1.41 g/cc (Ref 2); CA Registry No 22113-87-7
Gap Test. When 2g of MF were detoned 0.5cm from Methylamine Nitrate, there was no transm of the deton, but in contact with the MF there were 3 transmissions in 3 trials (Ref 2)
Hygroscopicity. When exposed to 50% humidity it absorbs 100% by wt of w in 21 days (Ref 2)
Impact Sensitivity. The 50% expln height is 2.5m (10kg wt) (Ref 2)
Power by Lead Block Expansion. 100% of PA (Ref 2)
Shock Sensitivity. It is detoned by 2g of MF when pulverized and packed to a d of 1.20g/cc.
It is also detoned by 20g of PA when packed to a d of 1.4g/cc in glass tubes (Ref 2)
Thermal Sensitivity. At 375–90° it decomps with burning in 6–5secs (Ref 2). In a 20mm tube combstn is difficult. It melts and boils before burning and only the heated material burns without propagation to unheated material. When unconfined it melts and boils without burning (Ref 1)
Mixtures of Methylamine Nitrate with Compounds which have Explosive Properties. A mixt with 70–80% AN is called “Nitramite No 2" in Fr (Ref 2). When detoned with 2g of MF in 30mm tubes it has a deton vel of 2550m/sec at a d of 1.00g/cc and 3250m/sec at 1.25g/cc (Ref 2).
Mixts of Methylamine Nitrate with AN, Ca nitrate, or Na nitrate form low melting euctectics which are castable expls (Ref 1) A soln of 200g of Methylamine Nitrate in 800 lbs of methyl alc is a useful fuel for turbojets (Ref 3). A 50/50 mixt by wt with hydrazine is a gas generator prophtl (Ref 4). Mixts with hydrazine and methylhydrazines are stable and hypergolic with liq O, N dioxide, red fuming nitric acid, white fuming nitric acid, and F (Ref 5). A compn of 46.8% AN, 33.3% Methylamine Nitrate, 16.7% w, 2.0% resin, and 1.2% guar gum, when boosted with 0.5 lb of Comp B, has a deton vel of 21000ft/sec and is a useful mining expl (Refs 6 & 7)

Methylamine Perchlorate, mw 255° with decmpn (Ref 2); it can be recrystd from et alc/ chlf mixts (Ref 4). The crystal structure by X-ray diffraction of the solid is given in Refs 2 & 5. There is a phase transition at 178°; d of phase II at 77°, 1.58g/cc; d of phase I at 200°, 1.58g/cc (Ref 2). The temp of expln is 338° (Ref 1); formn const in acetonitrile is 35 (Ref 3). By mass spectral analysis it was shown
that the vaporization, then thermal decomp betw 150° and 275° is primarily by dissocon into methylamine and perchloric acid plus a small amt by a more complex path leading to C and N oxides (Refs 4 & 6)


Methylamine Picrate, CH₃NH₂·C₆H₃N₃O₂⁺, C₇H₈N₃O₇, mw 260.17, N 21.54%, OB to CO₂ -67.7%; yellow crysts, 3 cryst forms: a trimorphous form at low temp which changes at 58° to a rhombic form, and at 63° to a 3rd form (Ref 2), mp 211° (cor) (Ref 4); α= 1.473, β= 1.878, γ= 1.987 (Ref 4). It is prep'd by the addn of methylamine to a satd (6%) soln of PA in w, recryst'd from aq ethyl alc (Ref 4); solv is 1.33 in 100p of w, fairly sol in ethyl alc (Ref 1). It behaves as a weak electrolyte in ethanolamine, but the conductivity is high (Ref 3)


Methylamine Picrolonate, CH₃NH₂.C₃H₁₀H₉N₄O₂⁻, C₁₁H₁₅N₄O₅, mw 295.25, N 23.72%, OB to CO₂ -127%; pale yellow crysts from w, decomps at 244° (Ref 3); solv at 16°, 1p in 1073p of w, 4717p of ethyl alc; at bp, 1p in 369p of w, 133p of ethyl alc (Ref 3); it exptds on rapid heating (Ref 2)

Refs: 1) Beil 24, 51 2) L. Knorr, Ber 30, 914 (1897) 3) J. Ootobi, ZPhysiolChem 43, 305 (1904) & JCS (Abstr) 88 (Pt 1), 126 (1905)

Methyl Ammonium Chloride Complex with Cupric Azide, MeNH₃Cu(N₃)₂, CH₆ClCuN₇, mw 215.15, N 45.58%; dark violet crysts, mp 150° with decomp

Refs: 1) Beil 4, 91 2) M. Straumanis & A. Cirulis, ZAnorgChem 252, 9 (1943) & CA 38, 3563 (1944)

Methyl Nitramine, reacts with diazonium salts to form ArN:NMeNO₂ which are yellow solids that ignite below their mp and decomp on standing at room temp (Ref 1). It reacts with activated olefns to form adducts of the type XCH₂CH₂NMeNO₂ where “X” is an activating group (Ref 2)


Written by C. H. McDonnell

N-Methylaniline and Derivatives

N-Methylaniline (Methylaminobenzene or Benzenamine, N-Methyl). CH₃NHCH₆H₅, mw 107.15, N 13.07%, OB to CO₂ -277%. Colorless liq which rapidly darkens in contact with air, f.p -57°, bp 196.25°, d₄ at 20° 0.98912 g/cc, RI at 20° 1.5684 (Ref 10), Qₗ -973.5 kcal/mole, Qₗ Qₗ 7.7. gas 20.4 kcal/mole (Ref 7), crit press 51.3 ± 0.5 atm (Ref 4, UV peak at ca 3650Å (Ref 2), IR spectrum is given in Ref 5; CA Registry No 100-61-8

Prepd by the action of methylating agents (methyl chloride, bromide, iodide, or sulfate) on aniline. This procedure gives a mixt with dimethylaniline which is difficult to separate by distn (see below for sep procedure) (Refs 1, 6 & 9). Pure samples are best prep'd by the methylation of acetanilide or benzanilide to the N-methyl compds followed by acid hyd. It has been prep'd commercially by the action of methyl alc on aniline in an autoclave under press and by the action of methyl amine on halobenzenes. For a summary of prepns see Refs 6 & 9. It may be separated from aniline and dimethylaniline by treatment of the mixt with benzenesulfonyl chloride. Dimethylaniline fails to react and is extd out with dil acid. Aniline forms benzensulfonanilide which is acidic and is removed by washing with dil base, leaving the N-methylbenzenesulfonanilide. Purified N-methylaniline is obtd by acid hyd (Ref 8). N-Methylaniline is used as an additive to raise the octane no of motor fuels (Ref 6), as a dyestuff intermediate (Ref 3), in the prepn of Tetryl (see below), and in the prepn of Methylcentralite (Encycl, Vol 2, C137-R)
Refs:  1) Beil 12, 135, (149), [79] & [240]  
2) H. Ley & G. Pfiaffer, Ber 54, 369 (1921)  
3) R.N. Shreve, "Dyes Classified by Intermediate" (Chemical Catalog Co, 1922), 336  
4) W. Herz & E. Neukirch, ZPhyChem 104, 363 (1923) & CA 17, 2979 (1923)  
5) J.W. Ellis, JACS 49, 350 (1927)  
6) E.C. Hughes et al, IEC 42, 787 (1950)  
7) G.N. Vriens & A.G. Hall, IEC 44, 2733 (1952)  
8) Shriner, Fuson, & Curtin (1956), 119  
9) Houben 11/1 (1957)  
10) ChemRubHdb (1974-51), C-119

Salts and Complexes of N-Methylaniline with Inorganic Compounds:

Complex with Cyanic Nitrate, (MeNHPh)₂ - Cu(NO₃)₂, C₁₄H₁₂CuN₄O₆, mw 401.86, N 16.66%, OB to CO₂ - 1488%; blue crystals, prepd by the interaction of the components in hot methylv al

Refs:  1) Beil 12, (240)  
2) A. Cirulis & M. Straumanis, Ber 76, 828 (1943)

Complex with Dionic Pentaazide ion, MeNH₂Ph₄⁺Cu(N₃)₆⁻, C₁₇H₁₆CuN₄, mw 445.29, N 50.13%; fine brown needles which decomp at 80° and deton sharply at 203°, prepd by the action of Na azide on the above nitrate complex

Refs:  1) Beil 12, (240)  
2) A. Cirulis & M. Straumanis, Ber 76, 828 (1943)

Perchlorate Salt, MeNHPh·HClO₄, mw 207.62, N 6.75%, OB to CO₂ - 116%; needles from ethylene dichloride/eth, mp 79° (Ref 2). It is prepd by the action of 57% aq perchloric acid on the amine in w. The burning rate btw 1 and 400atm is in Ref 3

Refs:  1) Beil - not found  
& CA 75, 5854q (1971)  
3) A.E. Fogel’zand et al, FizGorenyiVzryva 8, 257 (1972) & CA 78, 45833a (1973)

Salts and Complexes of N-Methylaniline with Organic Compounds:

3-Bromopicate, C₁₄H₁₁BrN₃O₇, mw 415.15, N 13.50%, OB to CO₂ - 94.5%; a yellow solid from et alc, mp 171-72° with decomp (Ref 3); prepd by the interaction of the components in hot abs ethyl alc (Ref 2)

Refs:  1) Beil - not found  
2) R.P. Mariella et al, JOC 26, 3219 (1961)  

3-Chloropicate, C₁₄H₁₁ClN₄O₇, mw 370.70, N 15.15%, OB to CO₂ - 105%; a yellow solid from et alc, mp 165-66° with decomp (Ref 3); prepd by the interaction of the components in hot abs ethyl alc (Ref 2)

Refs:  1) Beil - not found  
2) R.P. Mariella et al, JOC 26, 3219 (1961)  

3-iodopicrate, C₁₃H₁₁IN₄O₇, mw 462.10, N 12.12%, OB to CO₂ - 84.8%; a yellow solid from et alc, mp 158-59° with decomp (Ref 3); prepd by the interaction of the components in hot abs ethyl alc (Ref 2)

Refs:  1) Beil - not found  
2) R.P. Mariella et al, JOC 26, 3219 (1961)  

3-Dinitrobenzoate, C₁₄H₁₃N₃O₆, mw 319.27, N 13.16%, OB to CO₂ - 143%; a brown solid, mp 102.6-3.8°; prepd by the interaction of the components in hot abs ethyl alc. The salt is used to isolate and identify N-methylaniline

Refs:  1) Beil 12, (245)  
2) C.A. Buehler & J.D. Calfee, IEC, AnalEd 5, 351 (1934)

3,5-Dinitrobenzoate; light yellow crystals, mp 121.8°; prepd by the interaction of the components in hot abs ethyl alc. It is also used to isolate and identify N-methylaniline

Refs:  1) Beil 12, (245)  
2) C.A. Buehler et al, IEC, AnalEd 5, 277 (1933)

m-Ethylpicate, C₁₅H₁₄N₄O₇, mw 364.31, N 15.38%, OB to CO₂ - 136%; yellow crystals from methylv alc, mp 114-15° with decomp; prepd by the interaction of the components in methyl alc or ethyl alc

Refs:  1) Beil - not found  
2) R.P. Mariella et al, JOC 26, 3219 (1961)

Ethyl-2,4,6-trinitrobenzene Complex, C₁₃H₁₂N₄O₆, mw 348.31, N 16.09%, OB to CO₂ - 147%; red prisms, mp 44°

Refs:  1) Beil 12, 140  
2) G. Schultz, Ber 42, 2635 (1909)

Picate, C₁₃H₁₂N₄O₇, mw 336.26, N 16.66%, OB to CO₂ - 119%; yellow crystals from methylv alc, mp 144.5°; CA Registry No 14953-19-6

Refs:  1) Beil 12, (151)  
2) J. Meisenheimer, Ber 52, 1673 (1919)

2,2',6,6'-Tetranitro-4,4'-biphenol Complex, MeNHPh·[HOCH₂H₂(NO₂)₂]-2,6-4]₂, C₁₆H₁₂N₄O₁₉, mw 437.32, N 14.80%, OB to CO₂ - 120%; bright yellow crystals, prepd by the interaction of the components in hot benz

Refs:  1) Beil - not found  
2) G. Saito &
α,α′-Trifluoro-2,4,6-trinitrotoluene Complex, C₆H₅F₃N₃O₆, mw 388.26, N 14.42%, OB to CO₂ = 108%; yellow needles, mp 56–57°C; prep by mixing equimolar amounts of the components in ethyl alc.
Ref's: 1) Beil – not found 2) D.N. Gray et al, JCS 1960, 2243
2,4,6-Trinitrobenzoate, C₁₄H₁₂N₄O₈, mw 364.27, N 15.38%, OB to CO₂ = 114%; colorless crystals which lose CO₂ on heating to form the colored trinitrobenzene complex; prep by mixing equimolar amounts of the components in acetic.
2,4,6-Trinitro-m-cresol Complex, C₁₄H₁₄N₄O₇, mw 350.28, N 15.38%, OB to CO₂ = 128%; yellow crystals from ethyl alc, mp 127–28°C with decomp; prep by the interaction of the components in ethyl alc; CA Registry No 51010-15-2
2,4,6-Trinitrotoluene Complex, C₁₄H₁₄N₄O₆, mw 334.28, N 16.76%, OB to CO₂ = 138%; prep by mixing the components in hot ethyl alc, recryst from ethyl alc.
Ref's: 1) Beil – not found 2) A.K. Dwivedy et al, JChromatog 29, 129 (1967)
Trinitro-3,5-xylenol Complex, C₁₅H₁₄N₃O₇, mw 364.31, N 15.37%, OB to CO₂ = 136%; yellow crystals from methyl alc, mp 165–66°C with decomp; prep by the interaction of the components in ethyl alc; CA Registry No 51010-34-5
Azido and Azo Derivatives of N-Methylalanine
p-Azido-N-Methylalanine, p-MeNH₂C₆H₄N₃, C₆H₅N₄ mw 148.17, N 37.82%; crystals, mp 52°C; prep by the action of hydrazine hydrate on N-methyl-p-nitrosoaniline in aq Na carbonate. Upon exposure to light in thin layers, it turns red, then violet.
Ref's: 1) Beil 12, (429) 2) A. Angeli & A. Pieroni, AttiAccadLincei v 32, i, 151 (1923) & CA 17, 3487 (1923)
4-Methylamino-2',3',4'-trinitroazobenzene, C₁₃H₁₀N₆O₆, mw 346.26, N 24.27%, OB to CO₂ = 116%; yellow platelets, mp 274.5–5.0°C with decomp; prep by the action of methyl amine hydrochloride on 4-fluoro-2',3',4'-trinitroazobenzene in eth, yield 95.8%
Ref's: 1) Beil – not found 2) O. Neunhoffer & W. Ruske, Ann 610, 143 (1957)
Nitro Derivatives of N-Methylalanine
Nitro-N-Methylalanines, C₇H₈N₂O₂, mw 152.15, N 18.41%, OB to CO₂ = 168%. The following isomers are described in the literature:
N-Nitro-N-methylalanine, needles or leaflets from eth, mp 38.5–9.5°C, volatile in steam without decomp (Ref 1); CA Registry No 7119-93-9
2-Nitro-N-methylalanine, red needles with blue/violet reflections from petr eth, mp 37°C (Ref 2), decomp above the mp (Ref 13); CA Registry No 612-28-2
3-Nitro-N-methylalanine, reddish yellow needles or prisms from ethyl alc, mp 68°C (Ref 3); CA Registry No 619-26-1
4-Nitro-N-methylalanine, brownish yellow prisms with violet reflections, mp 150–51°C (Ref 4), decomp above the mp (Ref 13), Q₂ 924.3 kcal/mole (Ref 9); CA Registry No 100-15-2
It is prep by the action of methylene on 4-chloro-1-nitrobenzene (Ref 5); by the action of methyl iodide (Ref 6), or methyl sulfate on 4-nitroaniline (Ref 7); or by the hydrolysis of 4-nitro-N-methylformanilide with hot concd aq HCl (Ref 8). In a study of the effect of nitric acid concn on the prods of the nitration of N,N-dimethylalanine to form Tetryl, it was isolated in low yield by the action of nitric acid, d 1.046g/cc, plus Na nitrite on N,N-dimethylalanine (Ref 10). A eutectic mixt with N-ethyl-4-nitroaniline has been patented as a stablizer for NC (Ref 12). Studies at NPF indicate that 4-nitro-N-methylalanine is superior to Centralite, 2-nitrodiphenylamine, or Acardite in stabilizing NC.

Dinitro-N-methylanilines, C₃H₇N₂O₄, mw 197.15, N 21.32%, OB to CO₂ —110%. The following isomers are described in the literature:

_N,2-Dinitro-N-methylaniline_, bright yellow prisms, mp 70° (Ref 1)

_N,4-Dinitro-N-methylaniline_, bright yellow needles from benz, mp 142.5° (Ref 2); CA Registry No 16698-03-6. It is prepd by the alkylation of N,p-dinitroaniline with methyl iodide in alk soln (Refs 8 & 9). It is one compd isolated from aged NC propInts stabilized with N-methylp-nitroaniline. Hollingsworth at ERDE examined the reaction of nitrogen dioxide with this stabilizer in order to elucidate the mechanism of the formation of the compds isolated. He found that after 7 days at 35°, a good yield of N,4-dinitro-N-methylaniline was obtd; and postulated that it arose from the oxind of N-nitroso-4-nitroaniline (Ref 16)

_2,4-Dinitro-N-methylaniline_, canary yellow needles or monoclinic prisms from acet ac, mp 178° (Ref 3), Qₐ 885.5kcal/mole (Ref 10), a UV peak is at 3600Å which may be used to detect and determine it in crude Tetryl (Ref 13); CA Registry No 2044-88-4. It is one intermediate in the series of reactions which occur when N,N-dimethylaniline is treated with nitric acid resulting in the formation of Tetryl (see in the Encycl under Tetryl). If N,N-dimethylanilne is allowed to stand overnight in the presence of nitric acid (d 1.254—1.340g/cc), an almost quantiy yield of 2,4-dinitro-N-methylaniline is obtd (Ref 11). In addn Clarkson isolated it in 93% yield by the action of dilute nitric acid on 2,4-dinitro-N,N-dimethylaniline, and he treated it in 75% sulfuric acid with 98% nitric acid and obtd a 91.9% yield of Tetryl (Ref 17). As a possible raw material for an improved prep of Tetryl, its prep from methyl amine and 1-chloro-2,4-dinitrobenzene was studied in detail, including kinetics and economics of the reaction (Refs 12 & 18). It can be sepd from commercial Tetryl and identified by thin layer chromatography (Ref 19).

Specs for material used by the US Armed Forces for the prep of Tetryl are in MIL-D-20309 (23 Nov 1951) and include the following requirements:

- **Color** — Yellow to orange-yellow
- **Moisture** — Maximum, 0.2 percent
- **Acidity or alkalinity** — Maximum, 0.10 percent
- **Acetone insoluble** — Maximum, 0.20 percent
- **Ash** — Maximum, 0.20 percent
- **Inorganic chloride** — Maximum, 0.07 percent
- **Melting point** — Minimum, 176.5°
- **Granulation** — Thru No 10 US Std sieve; minimum, 99.5 percent

_T,5-Dinitro-N-methylaniline_, red needles from EtOH, mp 163° (Ref 4)

_2,6-Dinitro-N-methylaniline_, orange needles, mp 106–07° (Ref 5), Qₐ 895.35kcal/mole, Qₚ 2.45kcal/mole, Q₉ 6.55kcal/mole (Ref 15). It has been found as a by-prod in the prep of the 2,4-isomer (Ref 15). It has been sepd from other compds related to Tetryl by thin layer chromatography (Ref 19)

_3,4-Dinitro-N-methylaniline_, mp 156° (Ref 6)

_3,5-Dinitro-N-methylaniline_, orange-yellow needles, mp 158° (Refs 7 & 14)

Refs: 1) Beil 12, 697  2) Beil 12, 728
3) Beil 12, 749, (361), [406] & (1681)
4) Beil 12, 757, [413] & (1704)  5) Beil 12, 758 & (365)  6) Beil 12, [414]
12) A.G. Hill & K.H. Klipstein, AIChETransactions 42, 527 (1946) & CA 40, 4883 (1946)

_Trinitro-N-methylanilines_, C₃H₇N₃O₆, mw 242.15, N 23.14%, OB to CO₂ —72.7%. The following isomers have been reported in the literature:

_N,2,4-Trinitro-N-methylaniline_ (2,4-dinitrophenylmethyl nitrimine), light yellow hexagonal crys
from EtOH, mp 115° (Ref 14), Q^v 869.2 kcal/mole, Q^f -5.3 kcal/mole, Q^d -0.7 kcal/mole (Ref 16); CA Registry No 19092-03-6. It has been shown to be an intermediate in the prepn of Tetryl from N,N-dimethylaniline as it can be prepd from N,N-dimethylaniline or 2,4-dinitro-N-methylaniline by the action of 70% nitric acid in 90% yield (Reps 13 & 14); and can be nitrated to Tetryl with a mixt of 64% sulfuric acid, 15% nitric acid, and 21% w; yield 91.9% (Ref 14). It can be isolated from commercial Tetryl and identified by thin layer chromatography (Ref 21) *N*,*N*-Dinitro-N-methylaniline (2,6-dinitrophenylmethylnitramine), mp 110.8°, Q^2 874.9 kcal/mole, Q^v -10.8 kcal/mole, Q^d -6.1 kcal/mole (Ref 17)

2,3,4-Trinitro-N-methylaniline, mp 190°, prepd by the oxidn of 2,3,4-trinitro-N,N-dimethylaniline (Encycl. Vol 5, D1315) with Cr trioxide (Ref 2)

2,4,5-Trinitro-N-methylaniline, mp 199°, prepd by the action of 80% nitric acid on 2,5- or 3,4-dinitro-N,N-dimethylaniline (Reps 3 & 6); also in low yield by the nitration of 3-nitro-N,N-dimethylaniline at 30° (Ref 9)

2,4,6-Trinitro-N-methylaniline (N-methylpicramide), yellow needles from EtOH contg acid, mp 114.8° (Reps 4 & 7); the UV spectrum has a peak at 340 and a shoulder at 410–20° (Ref 19); CA Registry No 1022-07-7. It is prepd by the hydrolysis of the N-nitroso compd (see below) at 70–80° (Ref 5); by the action of concd sulfuric acid (Ref 8) or UV light (Ref 12) on Tetryl; by the action of methylamine on Ethyl Picrate (Ref 18) or Tetryl (Ref 7); or by the action of nitric acid (d 1.42 g/cc) at 0° on N,N-dimethylaniline (Ref 10). It is present in crude Tetryl and is the active dermattic agent in the latter (Ref 12). It can be isolated from crude Tetryl and identified by thin layer chromatography (Ref 21) Thermodynamic properties, Q^v 853.6 kcal/mole, Q^f 10.45 kcal/mole, Q^d 15.1 kcal/mole (Ref 15)

Explosive properties, impact sensy 120% of PA, power by Pb block expansion 74% of PA (Ref 11) Use, RDX (60 g) is stirred into 40 g of molten N-methylpicramide at 120° to give a castable expl, deton rate 7750 m/sec, vacuum stab better than Cyclotol (Ref 20)


Tetranitro-N-methylanilines (except Tetryl), C_7H_7N_2O_8, mw 287.15, N 24.39%, OB to CO_2 -47.4%. The following isomers have been reported in the literature, but their expl props have not been examined N_2,3,4-Tetranitro-N-methylanilene (2,3,4-trinitophenyl-N-methylnitramine), mp 122.5°; prepd by the nitration of 2,3,5-trinitro-N-methylaniline with nitric acid (concn unspecified) (Reps 1 & 3)

N_2,4,5-Tetranitro-N-methylaniline (2,4,5-trinitrophenyl-N-methyl nitramine), needles from nitric acid; mp 143.5°; prepd by nitration of 2,4,5-trinitro-N-methylaniline, or by the action of 90% nitric acid on 2,4,5-trinitro-N,N-dimethylaniline (Reps 1 & 3)

2,3,4,6-Tetranitro-N-methylaniline, mp 127°; prepd by the action of sulfuric acid on N_2,4,5-tetranoitro-N-methylaniline (Reps 2 & 3)


Pentanitro-N-methylanilines, C_7H_4N_3O_7, mw 332.15, N 25.31%, OB to CO_2 -28.9%

N_2,3,4,6-Pentanitro-N-methylaniline (2,3,4,6-Tetranitro-N-methyl nitramine, m-Nitrotetryl);
 needles or monoclinic prisms, mp 145—46° with decompn (Ref 2); Q_c 2551 cal/g, Q_f
-29.9 cal/g (Ref 4). It is prepd by heating N,N-dimethylpicramine with nitric acid (d 1.5 g/cc) (Ref 2), or by nitration of N-methyl-3-nitroaniline (Ref 3). It is found in crude Tetryl as it is formed from a small amt of N-methylaniline present in commercial N,N-dimethylaniline (Ref 7). The effect of its presence on the stability of Tetryl is discussed by Knowles (Ref 6); it can be removed from Tetryl by a Na carbonate boil, being converted to Na styrphate (Ref 5). A procedure for the degrad of m-Nitrotetrayl in Tetryl is described in Ref 10

*Explosive properties.* Impact sensy by FI test (Encycl Vol 6, F39) 48% of PA (Ref 9); by Kast app max fall of 2 kg wt for 0/6 shots 19 cm, min fall for 6/6 shots 36 cm (51—3 and above 60 cm resp for Tetryl) (Ref 6); power by Pb block expansion 120% of PA (Ref 9); by plate dent test — a mix of 80% m-Nitrotetrayl and 20% NG has the same effect as a mix of 80% PETN and 20% NG (Ref 8); thermal stability — when heated at 20°/min it expl at 175°, at 5°/min it expl at 162°; it evolves N oxides after 2 hrs at 60° (Ref 6)

*N,2,3,4,5,6-Pentanitro-N-methylaniline,* mp 132° with decompn, Q_c 2453 cal/g, power by Trauzl test 151% of TNT, by BalMort 143% of TNT (Ref 11). According to Lothrop (Ref 3) the compd prepd by Blancksma (Ref 3) and described by him as N,Ar-hexanitro-N-methylaniline is actually one of the above-titled comds. Lothrop, however, was unable to distinguish between the two possible structures for Blancksma’s compd


N,Ar-Hexanitro-N-methylaniline (N-Methyl-N-pentanitrophenylnitrinate, 2,5-Dinitrotetrayl). The compd prepd by Blancksma by nitration of 3,5-dinitro-N-methylaniline and claimed to be the above, was shown by Lothrop to be a pentanitro-N-methylaniline (see above)

**Nitro Nitroso Derivatives of N-Methylaniline**

**Nitro nitroso-nitromethanilines, C_7H_7N_2O_3, mw 181.15, N 23.20%, OB to CO_2 128%**

2-Nitro-N-nitroso-N-methylaniline (N-Methyl-2-nitrophenylnitrosamine), yellow crystals from EtOH, mp 36° (Ref 1)

3-Nitro-N-nitroso-N-methylaniline (N-methyl-3-nitrophenylnitrosamine), yellow crystals from EtOH, mp 68—70° (Ref 2); CA Registry No 18600:50:5

4-Nitro-N-nitroso-N-methylaniline (N-methyl-4-nitrophenylnitrosamine), needles from hot EtOH, mp 104° (Ref 3); CA Registry No 943:41:9. It is prepd by the action of nitrous acid on 4-nitroso-N,N-dimethylaniline (Ref 4), or by the action of nitrous acid on 4-nitro-N,N-dimethylaniline (Ref 5). In his research on the prepn of Tetryl from N,N-dimethylaniline, Hodgson found that the action of nitric acid (d 1.12 g/cc) in the presence of Na nitrate gave a low yield of 4-nitro-N-nitroso-N-methylaniline (Ref 6). It is probably present in aged NC proplnts stabilized with methyl centralite (Encycl Vol 2, C138 & Ref 7). It is formed in aged NC proplnts stabilized with N-methyl-p-nitroaniline, and is formed when the latter is treated with nitric oxide in wet dioxane (Ref 8)

4-Nitro-2-nitroso-N-methylaniline, green prisms from acet/w, mp 165—67° with decompn; prepd by the photolysis of N-(2,4-dinitrophenyl)-N-methyl-leucine (Ref 9)


**Dinitrotetrayl-N-methylanilines, C_7H_6N_4O_3, mw 226.15, N 24.78%, OB to CO_2 84.9%.** The following isomers have been reported in the literature:
2,4-Dinitro-N-nitroso-N-methylaniline (2,4- 
dinitrophenyl-N-methylnitrosamine), yellow 
needles, mp 83–85° (Ref 1). It is prepd by 
the action of nitric acid (d 1.3g/cc) and Na 
nitrite (Ref 5), or 70% nitric acid (Ref 9) on 
N,N-dimethylaniline. It has also been prepd 
by the addn of solid Na nitrite to 2,4-dinitro-N- 
methylaniline in 65% sulfuric acid (Ref 10). 
It is one intermediate in the prepn of Tetryl by 
the nitration of N,N-dimethylaniline (Ref 11). 
It is decomposed by heat (Ref 9), or rapidly in 
boiling EtOH to give 2,4-dinitro-N-methylaniline 
(Ref 12)

2,5-Dinitro-N-nitroso-N-methylaniline, 2,5- 
dinitrophenyl-N-methylnitrosamine, orange 
noodles or plates from EtOH; prepd by the 
action of 50% aq Na nitrite on 2,5-dinitro- 
N,N-dimethylaniline in aq HCl (Refs 2 & 8). 
2,6-Dinitro-N-nitroso-N-methylaniline (2,6- 
dinitrophenyl-N-methylnitrosamine), white 
noodles, mp 115–116°; prepd by the action of 
Na nitrite in acet ac on 2,6-dinitro-N-methyl- 
aniline (Refs 3 & 6)

3,4-Dinitro-N-nitroso-N-methylaniline (3,4- 
dinitrophenyl-N-methylnitrosamine), mp 108–99°, 
prepd by the action of nitric acid (d 1.37–40 
g/cc) contg nitrous acid on 3,4-dinitro-N,N- 
dimethylaniline (Refs 4 & 7)

Refs: 1) Beil 12, 757 & (364) 2) Beil 12, 
[413] 3) Beil 12, 365 4) Beil 12; 414 5) P. vanRomburgh & J.D. Jansen, K Akad- 
Wetenschappen 19, 955 (1911) & CA 5, 3045 
(1911) 6) R. Meldola & W.F. Holley, JCS 
107, 619 (1915) 7) M.J. Smit, Proc Acad- 
Sci Amsterdam 22, 523 (1920) & CA 14, 1970 
(1920) 8) W.G. Macmillan & T.H. Reade, 
JCS 1929, 2864 9) F.M. Lang, CR 226, 
1381 (1948) & CA 42, 7263 (1948) 10) C.E. 
Clarkson et al, JCS 1950, 1561 11) J. 
Glazer et al, JCS 1950, 2662 12) B.L., 
Holingsworth, JCS 1959, 2423

N-Nitroso-2,4,6-trinitro-N-methylaniline (N- 
methyl-2,4,6-trinitrophenyl-N-methylnitroso- 
nitrosamine, N-methyl-N-nitrosopticramide), C7H5N5O7, 
mp 271.15, N 25.83%, OB to CO2 –56.1%. Its 
expl props have not been investigated. Bright 
yellow leaflets or needles from EtOH, mp 
106.5° (Ref 1); prepd by the action of nitric 
acid on N-methylpicramide suspended in acet 
ac (Ref 2), or by allowing Tetryl to stand for 
24 hours in the presence of concd sulfuric 
acid (Ref 3). It is a by-prod in the prepn of 
Tetryl by the action of 70% (Ref 4) or concd 
(up to 99%) (Ref 5) nitric acid on N,N-dimethyl-
aniline

Refs: 1) Beil 12, 770, (371) & (1738) 2) E. 
Banberger & J. Müller, Ber 33, 103 (1900) 
3) F. Reverdin, Bull Fr 41 9, 43 (1911) & CA 
4, 1089 (1911) 4) F.M. Lang, CR 226, 
1381 (1948) & CA 42, 7263 (1948) 5) F.M. 
Lang, CR 227; 384 (1948) & CA 45, 3811e 
(1951)

Nitroso Derivatives of N-Methylaniline

N-p-Dinitroso-N-Methylaniline, p-ONC6H4NMMeNO, 
C7H7N3O2, mw 165.15, N 25.45%, OB to 
CO2 –150%; cryst lumps from et alc, mp 101° 
(Ref 2). It is prepd by the action of Na 
nitrite on p-nitroso-N-methylaniline in aq HCl 
(Ref 2). It ignites when held at 45–50° for 
7 hours; a mixt of 33 of N-p-nitroso-N-methyl-
aniline, 14.5 of Ca silicate, 33 of Amm bi-
carbonate, and 15.5 of w is stable at 45–50° 
for up to 82 hours (Ref 4). As a trade name 
"Elastopar" it is used as a modifier, accelerator, 
and cross linker for rubbers and plastics (Ref 
3). It is mildly carcinogenic, but otherwise 
the toxicity is low (Refs 5 & 6)

Refs: 1) Beil 12, 686, [366] & (1512) 2) O. 
Fischer & E. Hepp, Ber 19, 2992 (1886) 
3) H.M. Leerper et al, Rubberworld 135, 413 
(1956) & CA 51, 8467d (1957) 4) Anon, 
BritPl 981634 (1965) & CA 64, 3103 (1964) 
5) J.H. Weisburger et al, Naturwissenschaften 
53, 508 (1966) & CA 66, 965y (1967) 
6) Sax (1975), 284

Written by C. H. McDonnell

METHYL ANISOLE AND DERIVATIVES

Methyl Anisole (Methyl methoxy benzene or 
Methoxytoluene). CH3OC6H4CH3, mw 
122.17, OB to CO2 –261.93%. Three isomers 
exist:

Ortho (2-Methyl anisole), liq, fr p –34.1°, 
bp 171.8°, d 0.9798g/cc at 20/4°; RI 1.5161 
(Ref 1).

Meta (3-Methyl anisole), liq, fr p –55.92°, 
bp 176.5°, d 0.9716g/cc at 20/4° (Ref 2).

Para (4-Methyl anisole, p-Cresyl methyl ether, 
p-Methoxy toluene or Methyl-p-Cresol), colorl
liq, fr p −32.05, bp 177.05; d 0.9702g/cc
at 20/4° (Ref 3). Prepn & other props are in
Beil

Refs: 1) Beil 6, 352, (171), [328] & [1244],
ortho 2) Beil 6, 376, (186), [351] & [1297],
meta 3) Beil 6, 392, (1999), [375] & [1351],
para

Azido Methyl Anisole (Azido methoxy toluol,
Methoxybenzazid in Ger). CH₃.O.C₆H₄.CH₂.N₃,
mw 163.17, N 25.76%, OB to CO₂ −191.21%. Three
isomers exist:
Ortho (1,1-Azido methyl anisole), liq, bp 118°
at 14mm of Hg. Prepd from a mixt of N-
Nitroso-N(2-methoxy-benzyl)-hydrazine and dil
sulfuric acid by steam distn (Ref 1). Explodes
when heated quickly (Ref 1);
Meta (3,3-Azido methyl anisole), liq, bp 134°
at 28mm of Hg (Ref 2). Prepd from a mixt of
N-Nitroso-N(3-methoxy-benzyl)-hydrazine and
dil sulfuric acid by steam distn (Ref 2);
Para (4,4-Azido methyl anisole); prepn & props-
are in Beil

Refs: 1) Beil 6, (181), ortho 2) Beil 6,
(195), meta 3) Beil 6, (207), para

Mononitro Methyl Anisole (2-Nitro-4-methyl
anisole, 3-Nitro-4-methoxy-1-methyl benzol
or Methyl-[2-nitro-4-methyl phenyl]-ether).
CH₃.O.(NO₂)C₆H₃.CH₃, mw 167.18, N 8.38%,
OB to CO₂ −167.48%, pale yellow cryst, mp
8.9°, bp 274° (partial decomp), d 1.2025
g/cc at 25/4°, RI 1.5536; sl sol in eth (Ref 1).
Prepd by heating K₂-nitro-p-cresol with methyl-
iodide & methylal in a sealed tube at 100°
(Ref 1). Another prepn is given in Ref 2

Refs: 1) Beil 6, 412 2) S. Yura, A. Nagasaka,
(1952) & CA 48, 3031 (1954)

Dinitro Methyl Anisole (4-Nitro-2-nitromethyl
anisole, 3-Nitro-6-methoxy-4-nitrotoluol
or Methyl-[5-nitro-2-nitrophenyl]-ether).
CH₃.O.(NO₂)C₆H₃.CH₂.NO₂, mw 212.18, N
13.21%, OB to CO₂ −113.11%, cryst, mp
93–94°. Prepd from 4-nitro-2(idomethoxy)
anisole in ether-benzene soln by treatment for
3 days at RT with Ag nitrate. The sodium salt
explodes violently on heating

Refs: 1) Beil, not found 2) G. Bendy,
C.C. Culvenor, L.J. Goldsworthy, K.S. Kirby
& R. Robinson, JCS 1950, 1130–8 (1950) &
CA 44, 10720–21 (1950)

Trinitro Methyl Anisole (4,6-Dinitro-2-nitro-
methyl-anisole, 3,5-Dinitro-6-methoxy-nitro-
methyl toluol or Methyl-[4,6-dinitro-2-nitro-
methyl phenyl]-ether). CH₃.O.(NO₂)₂C₆H₃−
CH₂NO₂, mw 257.18, N 16.34%, OB to CO₂
−77.77%, cryst, mp 65–66°. Prepd from 4-
nitro-2(nitromethyl)anisole by slow addition
to a mixt of concd sulfuric-nitric acids (2:1)
at 0° (Ref 2). Explodes violently when heated
quickly (Ref 2)

Refs: 1) Beil — not found 2) G. Bendy,
C.C. Culvenor, L.J. Goldsworthy, K.S. Kirby
& R. Robinson, JCS 1950, 1130–8 (1950)
& CA 44, 10720–21 (1950)

2,4,6-Trinitro-5-Methyl Anisole (2,4,6-Trinitro-
3-methoxy-1-methyl-benzol or Methyl-[2,4,6-
trinitro-5-methyl-phenyl]-ether).
CH₃.O.(NO₂)₃C₆H₃.CH₃, mw 247.18, N
17.00%, OB to CO₂ −80.91%, cryst, mp 92°,
sol in conventional organic solvents (Ref 1).
Prepd by nitration of methyl-m-toly ether
using concd nitric acid (Ref 1). Other prepn
are listed in Refs 2 thru 5

Refs: 1) Beil 6, 365 & [388] 2) M. Giua,
GazzChimItal 49, 146–54 (1919) & CA 14,
1530–31 (1920) 3) H. Barbier, HelvChimActa
11, 157–61 (1928) & CA 28, 1339 (1928)
4) K.I. Bogacheva, JAC(USSR) 13, 1606–7
(1940) & CA 35, 3985 (1941) 5) I. Wender,
H. Greenfield, S. Metlin & M. Orekin, JACS
74, 4079–83 (1952) & CA 47, 6895–96 (1953)

Methyl Nitraminoanisole (2,4,6-Trinitro-3-
methylmethanitraminoanisole, Tetranitroanisolemethyl-
nitramine, m-Methoxytetrayl or 1-Methoxy-3-
methyl-nitraminopircrate).
CH₃.O.C₆H.N(CH₃)NO₂(NO₂)₃, mw 317.2,
N 22.08%, OB to CO₂ −52.96%, cryst, mp
96–97° (Ref 3). Prepd from 2,3,4,6-tetra-
nitrophelymethylnitramine and m-nitrotetryl upon
heating with methyl alcohol (Refs 1 & 2). The
expsn temp (187°) was obtd on heating the
sample at the rate of 5°/min, while a temp of
198° was detn by heating at the rate of 20°/
min (Refs 2 & 3). Impact sensitivity with the
Kast app, max fall for no detonation using a
10kg wt (6 shots) was 15–16cm vs 14cm for
Tetryl (Refs 2 & 3); thermal stability at 90°, evolves oxides of nitrogen in hrs (Refs 2 & 3)

Methyl Azide. See under Methane in this Vol

Methyl Borate (Trimethyl borate or Trimethoxy borine), \( \text{CH}_3\text{O}_3\text{B} \), mw 103.92, OB to \( \text{CO}_2 \) \(-115.47\), colorless liq, mp \(-29^\circ\), bp \(68^\circ\), d 0.92 g/cc at \(20^\circ\); vapor d 3.59. Prepn & other properties are given in Bell (Ref 1). Sax (Ref 2) lists this compd as a dangerous fire hazard when exposed to heat or flame. It reacts with \( \text{O}_2 \) or steam to produce toxic & flammable vapors, and vigorously with oxid materials.

Refs: 1) Bell 1, 287, (143) & [275] 2) Sax (1963), 883-R; (1968) 914-R

4-Methyl-2,6-Dinitrotetramethylene-2,4,6-
Triamine (Methyl-bis [methyl-nitraminomethyl] amine). \( \text{CH}_3\text{N(NO}_2\text{)}\text{CH}_2\text{N(CH}_3\text{)}\text{CH}_2\text{N(NO}_2\text{)}\text{CH}_3 \), mw 207.23, N 33.80%, OB to \( \text{CO}_2 \) \(-96.51\%), mp 64.5–65.5°. Prepn from methyl-nitramine, formaldehyde and methylamine. De-flags at 305°. Thermal stability at 100°, not acid in 300min; at 135°, acid in 105min. Hydrosolubility at 25°, loses 7.2% weight at 90% RH, gains 6.9% weight at 100% RH. Impact sensitivity using Brueton No 3 machine is 50% positive with 5Kgm weight at greater than 90cm. International heat test at 75°, loses 0.6% weight. Power by ballistic mortar is 95% TNT. Vacuum stability at 100° is greater than 12sec per 5g in 24 hours.

Refs: 1) Bell – not found 2) Blatt, OSRD 2014 (1944)

Methylenediisonitrosoamine. See under MEDINA in this Vol

Methylenedinitramine or Methylenedisonitramine. See under MEDINA in this Vol

(Methylenedioxy) Dimethanol Dinitrate. CH\(_2\)(OCH\(_2\)ONO\(_2\))\(_2\), mw 198.11, N 14.14%, OB to \( \text{CO}_2 \) \(-8.08\%), liq. Prepn from formaldehyde or trioxymethylene with mixed acid. Impact sensitivity FI is 6% of PA. Power by lead block test is 148% of PA, and the material is described as “not very powerful”. Chemically unstable and reactive with moisture

Refs: 1) Bell – not found 2) Blatt, OSRD 2014 (1944)

Methyleneglycoldinitrate. CH\(_2\)(ONO\(_2\))\(_2\), mw 138.04, N 20.3%, OB to \( \text{CO}_2 \) \(+34.8\%\); oily liq, bp 75–77° at 20mm; d 1.54g/cc; insol in w, sol in org compds. May be prepd (Refs 2 & 5) by nitration of formaldehyde soln at 5°. If the temp is allowed to reach 10°, a violent decompn may take place. The resulting product separates atop the spent acid as an oil, and can be purified by washing with w to obtain a stable product.

It is about 65% as powerful an expl as TNT, and nearly as sensitive to impact as MF. It is reactive with moisture; and not very stable.

Methyleneglycoldinitrate gelatinizes NC and cellulose acetate, and it is easily absorbed by kieselguhr. Travagli (Ref 3) proposed using it as a substitute for NG or ethyleneglycoldinitrate.


N-Methylethylenedinitramine. See under MeDNA in this Vol

N-Bromo-N'-Methyl-Ethylenedinitramine. Br.(O\(_2\)NN)CH\(_2\).CH\(_2\)(ONO\(_2\))\(_2\), mw 243.04, N 23.06%, OB to \( \text{CO}_2 \) \(-29.6\%), pale yellow cryst, mp 118–19° (decomp); sol in acet. Prepn from N-methyl-ethylenedinitramine dissolved in 9q KOH by adding liq bromine dropwise with stirring. Yield of w-washed ppt is 90%. Explosion temp is above 360°. Power is 101.2% (TNT=100%). Sensitivity to initiation is 6.6cm
METHYLGLUCOSIDE AND ITS TETRANITRATE

\[ \text{Methylglucoside (Methyl-\(\alpha\)-D-glucopyranoside)} \]
\[ C_{7}H_{12}O_{6} \quad \text{mp 168°, d 1.46g/cc.} \]

Solubility in w at 17°, 63% (w/w); in 80% alc 7.3%; in 90% alc 1.6%; insol in eth. Can be prepd by refluxing finely powd glucose with methanol-HCl (Ref 2) and by other methods (Ref 3). On nitrification it yields an expl tetrantrate (Ref 3).

**References:**
1. Beil 1, 179
2. W. Will & F. Lenze, Ber 31, 68 & 80 (1898)
3. Daniel (1902), 438 & 486
4. Davis (1943), 243
6. L. Médard, MP 33, 193-98 (1951) & CA 47, 10229 (1953)

\[ \text{\(\alpha\)-Methylglucosyl Trinitrate. See 1,2,3-Butanetriol Trinitrate in Vol 2, B371-L} \]

METHYLHYDANTOIN AND DERIVATIVE

\[ 5\text{-Methylhydantoin (2,5-Dioxo-4-methylimidazolidine).} \]
\[ \text{C}_{7}\text{H}_{10}\text{N}_{2}\text{O}_{4} \quad \text{mw 154.14, N 24.55%; mp 140-142°.} \]

Sol in w, alc, acet; sl sol in eth. Exists as monohydrate and anhydrous salts, the former is formed on slow crystn from w, and the latter on rapid crystn. Both salts are white. Can be prepd by boiling 3g of inactive \(\alpha\)-ureidopropionic acid.

**References:**
1. Beil 24, 279 & (305)
2. Franchimont & E.A. Klobbie, Rec 7, 14 (1888)
3. H.D. Dakin, JCS 107, 439 (1915)
5. R. Adams & C.S. Marvel, OSRD Rept No 96, Serial No 23 (Aug 24, 1941), pp 8 & 22

1-Nitro-5-Methylhydantoin (3-Nitro-2,5-dioxo-4-methylimidazolidine).
H₃C.CH.NHCO.N(NO₂)₂.CO; mw 159.10, N 26.41%; OB to CO₂ -65.4%; colorless plates, mp 148-149.5°, bp, degrades above 225° giving a brown solid which chars on further heating, does not detonate even on heating to 360°. Sol in w, especially hot; decomp slowly in boiling w, sol in alc; nearly insol in eth, chlf and benz. Its aq soln is acidic (pH 4)

Can be prep'd by evapg 5-methylhydantoin (15g) dissolved in white, 99% nitric acid (50 ml) to dryness on a steam cone. The resulting residue (19.5-20g or 93-95% of theory) was recryst from hot, not boiling, w. The yield of purified product was only 65% of theory (Refs 1, 2 & 3)

Nitromethylhydantoin is an expl comparable to TNT in its sensitivity to impact. Qₓ = -448.8 kcal/mole; Qᵧ = -99.9 kcal/mole. It is slightly hygroscopic, and its stability to heat is inadequate


N-METHYLHYDROXYACETAMIDE
AND DERIVATIVE

N-Methylhydroxyacetamide (N-Methylglycolamide, N-Oxymethyl-Acetamide, Methylol-Acetamide). CH₃.CO.NH.CH₂.OH, mw 103.12, N 27.17%, OB to CO₂ -116.37%, very hygroscopic, mp 50-52°. Very slightly sol in w, alc, chlf; sl sol in glycerin. Prep from acetamide and KOH dissolved in formaldehyde and heated. Can be nitrated to form a powerful expl, N-Nitro-N-Methylhydroxyacetamide Nitrate (see below)

Ref: Beil 2, 178

N-Nitro-N-Methylhydroxyacetamide Nitrate
(N-Nitro-N-methylglycolamide nitrate).

O₂.NO.CH₂.CO.N(NO₂)₂.CH₃; mw 179.09, N 23.46%, OB to CO₂ -22.3%; white needles, mp 80.82°, bp (subl at 120-21° at 6mm); d 1.65 g/cc (room temp), 1.42g/cc (at 85°). Puffs off mildly and catches fire at about 220°, but does not expl even when heated to 360°. Was prep'd (Ref 2, p 31) by slowly adding 10g of N-methylhydroxyacetamide to 50ml of white nitric acid (99%), warming the soln at 50-60° for 1 hour, allowing to cool to RT, and pouring onto cracked ice. The residue was collected on a filter, washed thoroughly with cold w and dried. Yield 16-16.5g (80-83% of theory) of crude product. In order to purify it, the crude product was dried in about 150ml of 4:1, by vol, chlf-petr eth mixt

It is an expl, more powerful than TNT (about 133% by Ballistic Mortar), and comparable to Tetryl in sensitivity. Its Vel of Deton is 7420 m/sec at d 1.5g/cc, and 5490m/sec at d 1.0g/cc. Qₓ is about 380kcal/mole. It is practically non-hygroscopic and its thermal stability is satisfactory. Has been used by DuPont Co as a base charge for some detonators


α-Methyl-D-Mannosite (D-α-methylmannosite). C₇H₁₄O₆; mw 194.18; wh needles from 96% alc, or rhombic prisms, mp 193-94°, d 1.473 g/cc. Sol in w (24.6g/100p at 17°), sl sol in alc (1.5p/100p in abs alc and 3.2p/100p in 90% alc at 17°). On nitration, it yields the expl tetrinitrate

α-Methylmannosite Tetrinitrate (Nitro-α-methylmannosite). C₇H₁₀O₄(NO₂)₄; mw 374.18; N 14.97%; OB to CO₂ -21.4%; fine, asbestos-like needles; mp 36°. Was prep'd by Will and Lenze (Ref 2) by dissolving α-methyl-d-mannosite in cold concd nitric acid and adding concd sulfuric acid dropwise with stirring. It is an expl which is relatively stable at 50° (weight loss 1.3% in 10 days, 7% in 12 days)

Refs: 1) Beil 1, 907 & 908 2) W. Will & F. Lenze, Ber 31, 80 (1898) 3) Daniel (1902), 438 & 486 4) Davis (1943), 243

METHYLMERCURIC SALTS

Several salts contg the CH₃Hg⁺ group were prep'd by various investigators, and the following proved to be expl:
Methylmercuric Azide (Mercuric methylazide). CH₃HgN₃; crysts from alc; mp 130.5°; decomps explosively ca 200°. Was prepd by Perret & Perrot (Ref 3) by treating methyl mercuric hydroxide, CH₃HgOH (Ref 1) with hydrazoic acid.

Methylmercuric Chromate. CH₃HgCrO₄; crysts; decomps explosively ca 255–60°. Was prepd by the reaction of chromic acid with methyl mercuric hydroxide (Ref 3).

Methylmercuric Nitrate. CH₃HgNO₃; leaflets; mp 100°; v sol in w. Was prepd by Strecker (Ref 2) by treating methylmercuric hydroxide with nitric acid. It has to be handled with care, being a severe skin irritant.

Methylmercuric Perchlorate. CH₃HgClO₄; crysts; deflagrates ca 180°. Was prepd by treating methylmercuric hydroxide with 60% perchloric acid (Ref 3). Refs: 1) Beil 4, 681, (613) & 2) A. Strecker, Ann 92, 79 (1854) & 3) A. Perret & R. Perrot, Helv 16, 848–57 (1933) & CA 27, 4772 (1933)

2-Methyl-2-Methylol-1,3-Propanediol. Same as Metriol (see in this Vol) or Pentaglycerin.

METHYLNAPHTHALENE AND ITS DERIVATIVES

C₁₀H₈CH₃, mw 142.19. There are two isomers, both of which may be nitrated to contain as many as four nitrogroups. The di- and trinitroisomers are weak explosives.

Alpha-(or 1-) Methylnaphthalene

```
    1
   / \  
  8   7
     /|
    CH₃/ \\

8     1
6     2
5     3
```

Oil, mp ≈22°, bp 244.6°, d 1.0202g/cc at 20/4°, RI 1.6170 at 20°. Insol in w, v sol in alc & eth; sol in benz. Compd can be obt'd from fractions of coal tar.

Beta-(or 2-) Methylnaphthalene. Monoclinic cryst, mp 34.58°, bp 241.05°, d 1.0058g/cc at 20/4°, RI 1.6019 at 20°. Insol in w, v sol in alc & eth; sol in benz. Compd can be obt'd from fractions of coal tar.

Ref: Beil 5, 566, 567, (265, 266), [460, 463] & [1620, 1627]

Dinitromethylnaphthalenes. (O₂N)₂C₁₀H₈CH₃, mw 232.19, N 12.07%, OB to CO₂ —151.60%. The following isomers are described by Bedstein. These compds are weaker exps than the corresponding dinitronaphthalenes (see under Naphthalene and its Derivatives in this Vol)

2,4-Dinitro-1-Methylnaphthalene, mp 161°, gold needles from alc. Prepn from [2,4-dinitronaphthyl(1)] acetate by heating above its mp. Refs: 1) Beil 5, [463] & (1626) & 2) V. Veselý & L.A. Pastak, BullFr [4], 37, 1448 (1925)

4,5-Dinitro-1-Methylnaphthalene, mp 142–43°, needles from alc. Prepn from 5-nitro-1-methylnaphthalene by nitration on a steam bath using nitric (d 1.52g/cc) & concd sulfuric acids in glc AcOH & Ac₂O. Ref: Beil 5, (1626)

4,8-Dinitro-1-Methylnaphthalene, mp 122–23°, gold needles from alc. Prepn from 8-nitro-1-methylnaphthalene by nitration on a steam bath using nitric (d 1.52g/cc) & concd sulfuric acids in AcOH. Ref: Beil 5, (1627)

4, X-Dinitro-1-Methylnaphthalene, mp 176°, brown plates from AcOH. Prepn from 4-nitro-1-methylnaphthalene by nitration in the cold with nitric acid (d 1.5g/cc). Ref: Beil 5, (1627)

X,X-Dinitro-1-Methylnaphthalene, mp 168°, needles from benz. Prepn from 1-Methylnaphthalene by nitration with fuming nitric acid at 0°. Ref: Beil 5, (1627)

1,5-Dinitro-2-Methylnaphthalene, mp 131°. Si sol in alc & AcOH. Prepn (together with 1,8-dinitro-2-methylnaphthalene) from 1-nitro-2-methylnaphthalene by heating with concd nitric & acetic acids on a w bath. Refs: 1) Beil 5, [466] & (1635) & 2) V. Veselý & J. Kapp, Rec 44, 373 (1925)

1,8-Dinitro-2-Methylnaphthalene (1,X-Dinitro-2-methylnaphthalene; ”eso”), mp 209°. Si sol
in AcOH & alc. Prep from 1-nitro-2-methyl- 
naphthalene by heating with anhydrous nitric 
acid in presence of acetic & sulfuric acids 
Refs: 1) Beil 5, 568, (267), [466] & (1635)  
2) R. Lesser & G. Aczel, Ann 402, 32 (1914)  
3) V. Veselý & J. Kapp, Rec 44, 373 (1925)  
4) Urbanški 1, 447 (1964) 

Trinitromethylnaphthalenes, \((O_2N)_3C_10H_4.CH_3\), 
\(mw\ 277.19\), N 15.16%, OB to CO\(_2\) -112.60%. 
Trinitromethylnaphthalenes are supposed to be 
less powerful exps than trinitronaphthalenes, 
but comparable to dinitronaphthalenes 

2,4,5-Trinitro-1-Methylnaphthalene, mp 170°, 
gold cryst from benz or alc. Prep from 4,5- 
dinitro-1-methylnaphthalene by heating with 
nitric acid (d 1.5g/cc) 
Ref: Beil 5, [1627] 

4,4,5-Trinitro-1-Methylnaphthalene, mp 180–81°, 
straw-yellow needles from CCl\(_4\), V sl sol in alc, 
appreciably sol in CCl\(_4\), chl & AcOH. Prep 
from 4-nitro-1-methylnaphthalene by nitration 
with mixed nitric-sulfuric acids 
Refs: 1) Beil 5, (266)  2) R. Lesser & A. 
Glaser, Ann 402, 14 (1914) 

X,XX,XX-Trinitro-2-Methylnaphthalene, mp 182°, 
cryst from benz. Prep from 2-methylnaphtha 
elene in glac AcOH by nitration at 0° with 
fuming nitric acid 
Ref: Beil 5, [1635] 

NOTE: Nitroderivatives of 2-methylnaptha 
elenes have been described in detail by V. 
Veselý & J. Kapp in a series of articles: 
ChemiListy 18, 201–5, 244–9 (1924) & CA 
19, 2487 (1925); Rec 44, 360–75 (1925) & 
CA 19, 2948 (1925) 

1,6,8-Trinitro-2-Methyaminonaphthalene. 
\((O_2N)_3C_10H_4.(H)N(CH_3)\), mw 292.23, N 
19.18%, OB to CO\(_2\) -109.50%, cryst, mp 
259° (decomp). Prep from 1,6,8-trinitro- 
2-methoxy-naphthalene by heating with methyl 
amine in alc 
Refs: 1) Beil – not found  2) E.J. Van der 
Kam, Rec.45, 564–81 (1926) & CA 21, 82– 
83 (1927) 

Tetranitro-2-Methylnaphthalene. 
\((O_2N)_4C_10H_4.CH_3\), mw 322.21, N 17.39%, 
OB to CO\(_2\) -85.04%, needles from glc AcOH, 
mp 262–63° (decomp). Sol in glc AcOH, 
acet, dioxane & py; sl sol in benz, toluene, 
xylene & amyl alc. Prep from 1-nitro-2- 
methylnaphthalene by nitration using mixed 
acids of nitric (d 1.52g/cc), sulfuric (d 1.84 
g/cc) & oleum (20–25% SO\(_3\) free), and heating 
for one hour at 80° on a water bath. Two 
other isomers which do not decompose are 
prepd simultaneously; viz, mp (I) 230° & 
(II) 241–42°. Yield of the decomposed isomer 
is 3.23% 
Refs: 1) Beil – not found  2) M. Civera & 
C. Torello, Gazz 86, 350–57 (1956) & G.R. 
Loehr, PicArsnTrsln No 18 (1957) 

1-Methylidio Nitronaphthalene. 
\((I)CH(NO_2)_2.C_10H_7\), mw 313.10, N 4.47%, OB 
(smaller needle from CCl\(_4\), mp 74°. 
Decomp occurs at 110–35°. Prep from 1- 
nitromethylnaphthalene by reacting it at 0° 
with a w soln of iodo K iodide & NaCl 
Ref: Beil 5, [1626] 

2-Methylidio Nitronaphthalene. 
\((I)CH(NO_2)_2.C_10H_7\), mw 313.10, N 4.47%, 
OB to CO\(_2\) -122.64%, cryst, mp 60°, decomp 
at 105°. Prep from 2-nitromethylnaphthalene 
by reacting it at 0° with a w soln of iodo K 
iodide & NaCl 
Ref: Beil 5, [1635] 

Methylnitramine (Nitraminomethane). 
CH\(_3\)NH\(_2\)NO\(_2\) or CH\(_3\)N:N(NH\(_2\))\(_2\)OH; mw 76.06, 
N 36.83%, OB to CO\(_2\) -42.1%; colorless needles 
from ether; mp 38°; d 1.243 at 49/4°; RI 
1.4616 at 48.6°. V sol in cold w, alc, chl 
and benz; less sol in eth and still less sol in 
petr eth. Can be prep from nitrotating n-methyl-
urethan with abs nitric acid. The resulting 
soil of methyl nitrourethane is drowned in w, 
neutralized with Na carbonate, and extrd with 
eth to remove methyl nitrourethane. On 
passing ammonia gas thru the eth extract, a white 
ppt of the ammonium salt of methylnitramine 
is deposited and sep by filtration. It is disd 
in alc and boiled to drive off the ammonia, and
to conc to a small vol. The resulting syrup is placed in a vacuum desiccator over sulfuric acid, where the final drying takes place. To obtain a purer product, the deposit may be cryst from eth.

Methyleneimine explodes on heating or on contact with conc sulfuric acid. Based on tests conducted in the USA during WWII, it is more powerful than TNT (144% as detd by Trauzl lead block test) (Ref 3).

Being a strong monobasic acid, it easily forms metallic salts, some of which are exl, as for instance:

**Potassium Methyleneiminate**. K.CH₃O₂N₂; fine needles, which expl violently on heating. According to Davis (Ref 2), the heavy metal salts of methyleneimine are primary explosives, but have not been investigated extensively. Refs: 1) Bell 4, 567, (568) & [968] 2) Davis (1943), 371–72 3) Blatt, OSRD 2014 (1944)

3-Methylnitramino-2,4,6-Trinitro-Phenetole
(Methyl-[2,4,6-trinitro-3-ethoxy-phenyl] nitramin, 2,4,6-Trinitro-3-methylnitramino-phenol ethyl-ether). O₂N,N(CH₃)₂C₆H(NO₂)₃O.C₂H₅, mw 331.23, N 21.15%, OB to CO₂ -65.21%, colorless cryst, mp 98–99°. Sol in methanol. Prepn from methyl(2,3,4,6-tetranitro-phenyl)-nitramin by boiling with et alc. Expln temp is 192–202° (Ref 1). Ignition temp is 202°. Impact sensitivity with a 10kg weight is 16–19cm. Stability test at 90° showed decomp after 2 hours (Refs 1, 2 & 3). Decomps is shown after 20 weeks at 50° (Ref 1).


**Methyl Nitrate** (Methylnitrat or Salpetersäure-methylester in Ger). CH₃ONO₂, mw 77.04, N 18.18%, OB to CO₂ -10.4%; colorless, mobile volatile liquid with odor of chlf; d 1.203g/cc at 25° & 1.21g/cc at 15°; fr p below -20°, bp ca 65°; vap d 2.66g/cc (Air 1.0g/cc); its vapors expl when overheated. V sl sol in w (3.85g at 20°) and miscible with alc or ether; easily gelatinizes colloidin cotton. Was first prepd in 1862 by C. Lea by distilling methanol with 63% strong nitric acid in the presence of urea nitrate, but the yield was small (See Ref 1, p 284). Delépine (Ref 2) prepd it, 36% yield, by dissolving methanol in sulfuric acid (d 1.84g/cc) and adding this soln gradually to mixed nitric-sulfuric acid. A.P. Black & F.H. Beber improved Delépine’s method and obtd MeN in yields up to 80% (See Ref 4, pp 62–63). Laboratory method of prepn is given in Ref 3, pp 203–04.

Desseigne developed in France, after WWII, both batch and continuous methods which are claimed to give yields up to 90% (Ref 8, pp 62–63).

**Procedure for Batch Method.** Introduce into a 3-neck round-bottom flask of 350ml capacity (provided with an agitator and a cooling ice-water bath), 138g of mixed-acid of approx compn: HNO₃ 50.6, H₂SO₄ 45.7 & H₂O 3.7%. The acid was prepd by mixing with stirring & cooling, calcd units of concd nitric (94–98%) and sulfuric acids (d 1.84g/cc). After cooling the mixed acid in the flask to below 30°, introduce drop by drop 32g of methanol contg ca 1g of urea, while stirring and cooling. Continue agitation and cooling until the temp drops to ca 18°. Transfer the mixt to a separatory funnel in which stopcock and glass stopper are carefully greased (to avoid an expln by friction to which MeN is very sensitive). After separating the layers, remove the bottom (acid) layer and discard it. Wash the contents of funnel first with 20ml of iced w and then with 20ml of 2% Na carbonate. Dry MeN with anhyd Na carbonate and transfer to weighing bottle. Desseigne obtb 69g, which is an 89.5% yield.

In the continuous process, also developed by Desseigne, a special apparatus is used. A detailed description of the process together with drawings of app are given in Ref 8, pp 63–8. The product prepd by Desseigne boiled at 65.2°, its d was 1.210g/cc at 20° and soly in w 3g in 100g (Ref 8, p 63).

Roig (Ref 9) describes the method of prepn in which MeN is obtd as a 60% soln in methanol. This is done in order to avoid any risk of expln during nitration. Detailed descriptions of both laboratory and semi-plant production are given in Ref 8, p 166. The yield of MeN is 77% in lab practice and 83.7% in semi-plant production (Ref 8, p 164).
Explosive Properties of MeN (Refs 3, 5, 6, 7, 11 & 12)

Brisance by Lead Block Compression Test 132% NG

Decomposition Equations. Acdg to Berthelot, the decomposition of MeN may proceed either as:

\[ 2\text{CH}_3\text{ONO}_2 = \text{CO}_2 + \text{CO} + 3\text{H}_2\text{O} + \text{N}_2 \]  

or as:

\[ 2\text{CH}_3\text{ONO}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{H}_2 + \text{N}_2 \]

Based on the heat of formation of 39.6 kcal/mole, Berthelot calc'd heats of expn at constant volume \((C_v)\) and with \(\text{H}_2\text{O}\) liquid, as:

1609 kcal/kg for equation (1) and 1616 kcal/kg for equation (2). As the value detd at the same time for NG is 1595 kcal/kg, it is apparent that MeN has slightly higher energy content than NG.

Detonation Velocity. When detd in glass or metal tubes of small diam (3 to 5 mm), the values are low, ranging from 1890 to 2482 m/sec, vs 1500 m/sec for NG. When detd with a glass tube 20 mm diam and 1 mm wall thickness, the value is 6600 m/sec. Acdg to Naofm (Ref 3, p 206), values up to 8000 m/sec should be obtd in tubes 30-40 mm diam. These values are comparable for those for NG (Ref 3, p 145). 

FI (Figure of Insensitiveness) = 29% PA (Ref 6)

Ignition & Explosion of MeN by Flame. When MeN in an open dish is brought in contact with a flame, it ignites immediately and burns quietly with a large non-luminous flame. The vapors puff readily on ignition, and on heating them to 150°, they explode. When a small amt of MeN is ignited in a narrow glass vessel with a safety fuse, it sometimes gives a puff accompanied by breaking the glass into large pieces; sometimes a brisan detonation takes place accompanied by pulverizing the glass to a fine powder (Ref 3, pp 205-06)

Impact Sensitivity, by Kast apparatus with 2 kg wt, it explodes at 40 cm drop, vs 4 cm for NG. Even when mixed with kieselguhr it is less sensitive than NG (Compare with FI)

Initiation Sensitivity. See Sensitiveness to Initiation

Power, by Ballistic Pendulum 20% PA (Ref 6)

Power, by Trauzl Test. For 10g sample with water tamping, the expansion is 615 cc vs 600 cc for NG, which gives ca 102.5% NG. When mixed with kieselguhr, or gelatinized with NC, MeN gives about the same values in the lead block as corresponding mixts of NG, namely 320 & 565 cc. Blatt (Ref 6) gives a value of 174% PA.

Sensitivity to Flame. See under Ignition and Explosion of MeN by Flame

Sensitivity to Initiation. MeN is more sensitive than NG. For example, when it is inititated with a No 1 cap, under w tamping, the detonation effectiveness is equal to 88% of that with a No 8 cap, while NG under the same conditions gives only 33% effectiveness.

Toxicity and Fire & Explosion Hazards are briefly discussed in Refs 11 & 12.

Uses: It can be used as a gelatinizer of colloid cotton in commercial expls, but its high volatility is objectionable (Ref 2, p 208). Has been used in some rocket proplnts (Refs 11 & 12)

Method of analysis of MeN is described by Vandoni (Ref 10)

Written by B.T. FEDOROFF


Methyl Nitrite (Methylnitrit or Saltpetrigäure methylester in Ger), CH₃ONO₂; mw 61.04, N 22.95%; colorless gas which liquefies at -12 to -16° and freezes below -19°, d 1.00g/cc at -19°; miscible with alc or ether. Was first prepd in 1854 by A. Streckel by the action of nitric acid on bromide (dimethoxystrychnine); he also prepd it by the action of nitric acid on methanol in the presence of either Cu or As₃O₃ (See Ref 1, p 284). More recent methods include treating methanol with isoamyl-nitrite (drop by drop) or by treating methanol with inorganic nitrates in presence of sulfuric acid (Ref 1). Adickes (Ref 2) describes a special apparatus in which is achieved automatically the complete mixing of qq alc-NaNO₂ and H₂SO₄
soin in order to avoid the sudden dangerous evoln of gas during nitrification. Its toxicity and fire and expln hazards are given in Ref 3. Severe explosion risk when shocked or heated! Refs: 1) Beil 1, 284, (141), [273] & (1201) 2) F. Adickes, JPraktChem 161, 275 (1943) & CA 38, 65 (1944) 3) Sax (1957), 902 4) CondChemDict (1971), 579-L

METHYLNITROGUANIDINE AND ITS DERIVATIVES

N-Methyl-N'-Nitroguanidine. 
H₃C.NHC(:NH).NH.NO₂, mw 118.10, N 47.44%, OB to CO₂ 67.7%, mp 159–61°, colori crysts. McKay and Wright (Ref 7) prepd it by heating Nitroguanidine (10.4g), diss in 30g of w containing 12g of potassium hydroxide, to 40°, and adding gradually with stirring, 13.5g of methylamine hydrochloride. This gave a viscous sludge, and some ammonia was evolved. The temp was raised steadily to 59–61° over a period of 8 minutes, and held there for 23 minutes while stirring the mixt continuously. After the mixt was cooled to 6°, a white ppt of methylnitroguanidine (MeNGu) was filtered off, washed with 30ml of cold w and dried. The crude product weighed about 10g (84.7% yield) and melted at 151–54°. Purification of the product was achieved by crystn, f 1st from hot w (3ml per g) and then from 95% ethanol (8ml per g) As an expl, it is less powerful and brisant than Picric Acid (Ref 6). It has been used for the prepn of the following expl derivatives:

N-Methyl-N'-Nitroguanidine Nitrate. 
H₃C.NHC(:NH).NH.NO₂.HNO₃, mw 181.12, N 38.67%, OB to CO₂ 22.1%, mp 87–91°, colori crysts. McKay and Wright (Ref 7) prepd it by adding 0.355ml of 99% nitric acid, over a period of 4 minutes, to a constantly-stirred suspension of 1g of finely ground MeNGu in 10ml of carbon tetrachloride at 5°. The gummy suspension was cooled to 15° and stirred for an additional 15 minutes. This gave a granular ppt of crude nitrate, which weighed after drying, an average of 1.42g (93% yield). Its mp varied with each preparation. It is an expl which can detonate on impact

N-Methyl-N'-Nitroguanidine Perchlorate. 
H₃C.NHC(:NH).NH.NO₂.HClO₄, mw 218.61, N 25.60%, OB to CO₂ 11.0%, mp 104°, needle-like rossettes. McKay and Wright (Ref 7) prepd it by dissolving (on heating) 6g of MeNGu in 25ml of 60% perchloric acid, and then cooling the soln to about 0°. This caused the pptn of needle-like rossettes, which were sep’d by filtrn, washed with 10ml of 30% perchloric acid and then with 10ml of carbon tetrachloride. The yield was 6.67g of salt, mp 98–101°. The pure product, mp 104°, was obtained on recrystn from w. The perchlorate was quite sensitive to impact, and detonated violently

Attempted Nitrtn of MeNGu: Various methods of nitrtn were attempted including nitric acid alone, or in combination with 100% perchloric acid, zinc chloride, perboric acid, boron trifluoride, etc. All of them gave MeNGu nitrate, described above, but no nitro derivatives (Ref 7, p 3029)

N-Methyl-N-Nitrosopyrrolo-N'-Nitroguanidine. 
H₃C.N(NO).C(:NH).NH.NO₂, mw 147.10, N 47.61%, OB to CO₂ 38.1%, mp 118° with decomp.; yld cristls; very sl sol in w, sol in methanol, decomp in alkaline soln with gas evolution. McKay and Wright (Ref 7) prepd it by dissolving 10g of MeNGu in 100ml of w to which was added 30ml of nitric acid (d 1.42 g/cc). After cooling the soln in an ice-w bath, 12.4g of Na nitrate diss in 20ml of w, were added over a 5 minute period with stirring. After stirring for an additional 20 minutes, the mixt was filtd, and the cryst crude ppt washed with cold w. The crude dried product weighed 11.25g (90.6% yield) and melted at 112–13° with decomp. It can be purified by crystn from methanol, giving a product with mp 118°, but the yield is very small. Its expl properties have not been examined

guanidines) 4) T.L. Davis & E.N. Rosenquist, ibid, 59, 2112 (1937) (Transformations of Nitrosofuranidine, Alkyl nitrosofuranidines and N-R, N'-Dialkylguanidines) 5) Davis (1943), 386 6) Blatt, OSRD 2014 (1944)
7) A.F. McKay & G.F. Wright, JACS 69, 3028 (1947)

2-Methyl-2-Nitro-1,3-Propanediol Dinitrate
(Nitroisobutyglycol dinitrate).
CH₃C.NO₂(CH₂ONO₂)₂, mw 225.14, N 18.67%, OB to CO₂ -24.87%, mp 38°, ignites above 240°. Prepd from the glycol by nitration with mixed acid, with 90% yield. Brisance, crushes 53g sand, equivalent to Tetryl. Q₁₅ is 531.4cal/mole. Impact sensitivity, FI 86% relative to PA, with Brueton No 5 machine, 50% positive with 5kg weight at 27–46cm, slightly more sensitive than TNT. Power by ballistic mortar is 134–38% TNT, 99.5% blasting gelatin; lead block expansion, 153% PA. Riffle bullet impact in welded cans gave 4/4 high order detonations. Thermal stability at 135°, acid in 15–30 minutes at 82.2°; heat test, 10 minutes at 82.2°. This material and its homologs from other aliphatic nitro compounds and aldehydeys have been suggested as substitutes for NG

Refs: 1) Bell - not found 2) F.H. Bergeim, USP 1691955 (1929) & CA 23, 708 (1929)
3) J.A. Wyler, USP 2195551 (1940) & CA 34, 5283 (1940) 4) Blatt, OSRD 2014 (1944)

2-Methyl-2-Nitro-1-Propanol (2-Nitro-2-methyl-1-propanol, β-Nitroisobutyl alcohol).
(CH₃)₂C(NO₂).CH₂OH, mw 119.12, N 11.76%, OB to CO₂ -127.60%, needles or plates from methanol, mp 90–91°, bp 94.5–95.5° at 10mm. Easily sol in ethyl & methyl ales, eth and w (350p in 100p at 20°). May be prepd by treating 2-nitropropane with formaldehyde in the presence of an alkaline catalyst, such as K bicarbonate (Refs 1, 2, 3 & 4). On nitration, it yields an exp1, 2-Methyl-2-Nitro-1-Propanol Nitrate (see below)

2-Methyl-2-Nitro-1-Propanol Nitrate (2-Nitro-2-methyl-1-propanol nitrate).

(CH₃)₂C(NO₂).CH₂ONO₂, mw 164.12, N 17.07% (nitrate N 8.54%), OB to CO₂ -68.20%, bp decomps in 5 sec at 200–05° without melting or detonation. Only liq, insol in w & petr eth; sol in alc, eth, acet, bz & CCl₄. May be prepd by siftng 50g of dry powdered 2-methyl-2-nitro-1-propanol into a mixt of 58.5g of 90.5% HNO₃ and 241.5g of 103.1% H₂SO₄ (oleum), while stirring the mixt and maintaining it at 15°. After the addition, stirring was continued for 1 hour, and the mass was allowed to stand for 1/2 hour. As no sepn took place, the mixt was poured over cracked ice. The bulk of the w was decanted and the oil transferred to a separatory funnel, where it was washed with w, Na bicarbonate, and again with w to neutrality to litmus. All the washings were mixed with the spent acid and extrd w eth. After washing the extr with w and evap the eth, the oil was added to the main product, and it was dried under vacuum

The yield obtained by Aaronson was 34.8g (50.5% of theory), and the product contained 16.99% (theoretical 17.07%) (Ref 5)

Methyl nitropropanolnitrate readily gelatinizes collodion cotton and, to a lesser extent, higher-nitrogen NC. Its explosive power is comparable to that of TNT, and about 75% of that of blasting gelatin. It is very insensitive to de- onation, and for this reason its sand test value could not be detd

Impact Sensitivity. > 100cm with 2kg weight or less sensitive than TNT

Thermal Stability. Unsatisfactory (about 6 minutes in the 82.2° Heat Test)

Toxicity. Comparable to NG

Uses. No military applications reported

4) C.L. Gabriel, IEC 32, 887 (1940) 5) H. Aaronson, PATR 1125 (1941), pp 1 & 4 and Table III

Methylnitrosobutyramide (Nitroso-methyl-n-Butyramid in Ger).

\[
\text{ON} \quad \text{CH₃.C₂H₅} \quad \text{C} = \text{O}
\]
N-Methyl-$N^\prime$-(2-Nitroxyethyl) Ethylene Dinitramine. See 1-Methyl-$N^\prime$-(2-Nitroxyethyl) ethylenedinitramine in Vol 5, D1377-R

N-Methyl-$N$-(2-Nitro propyl) Nitramine. (Me$_2$NENA; N-(2-Nitroxypropyl) methyl nitramine. (O$_2$N)(CH$_3$)$_2$(CH$_2$CH(ONO$_2$)$_2$.CH$_3$, mw 179.16, N 23.46%, OB to CO$_2$ -66.80%, pale yellow oil, mp 22-23°, d 1.320g/cc at 25/4°, RI 1.478 at 25°. Prep from 2-hydroxypropylamine after nitration with 98% nitric acid at 10° by reaction of the amine-nitric acid mixt with acetic anhydride & acetyl chloride at 35°. Reaction mixt poured on ice. Yield is 74%. No expl properties listed
Refs: 1) Bell - not found 2) Blomquist, OSRD 4134, 45 & 119 (1944)

3-Methylol-2-Butanol (2-Methyl-1,3-butanediol or α,γ-Diacyl-β-methylbutan-1)-alcohol). Ch$_3$.CH(OH).CH(2OH).CH$_3$, mw 104.15, viscous oil, bp 200° & 98-99° at 9mm. Sol in w, v sol in alc and eth. Can be prep by either reduction of the corresponding aldehyde, 2-methylbutan-1-al(1) with Al amalgam (Ref 1), or by electrolytic reduction in 10% sulfuric acid of the corresponding ketone alc. In the latter case, methyl-2-butalone-3-ol(1), obtained by the condensation of methylketone with formaldehyde, can be used. On nitration, it yields an expl dinitrate
Refs: 1) Bell 1, 482, (250) 2) L.P. Kyriakides, JACS 36, 535 (1914)

3-Methylol-2-Butanol Dinitrate.
CH$_3$.(CH(ONO$_2$)$_2$.CH(2CH(ONO$_2$)$_2$.CH$_3$, mw 194.15, N 14.43%, OB to CO$_2$ -74.17%, oily liq. Can be prep in about 62% yield by gradually adding 3-methylol-2-butanol to a mixed acid containing approx HNO$_3$ 25.3, H$_2$SO$_4$ 59.6 & w 15.1%. Temp of nitration, 5-10°; total nitration time about 30 minutes; ratio of HNO$_3$ to methylolbutanol, 1:5

The resulting compound was an expi, very volatile and very unstable (2 minutes in the 82.2° Abel test, compared with 10-15 minutes for NG). The impact sensitivity (BurMines, 2kg weight) was 100cm+. Because of its poor stability, it was not recommended for use as a military expl
Ref: K.S. Warren, PATR 1103 (1941), p 2 and Table II

3-Methylol-2-Butanone (β-Methyl-γ-ketobutanone). CH$_3$.CO.CH(2OH).CH$_3$, mw 102.13, color, liq, mp does not freeze at -80°, bp 90° at 17mm, d 0.99g/cc, RI 1.4320, sol in w. Can be prep by condensation of methyl ethyl ketone with 1 mole of formaldehyde (Refs 2 & 3). On nitration, it yields an expl.

3-Methylol-2-Butanone Mononitrate (β-Methyl-γ-ketobutanone mononitrate). CH$_3$.CO.CH(2CH(ONO$_2$)$_2$.CH$_3$, mw 147.13, N 9.52% (theory), 8.20% found; OB to CO$_2$ -114.18%; liq. Prep by nitrating methylolbutanone with mixed acid (HNO$_3$ 25.3, H$_2$SO$_4$ 59.6 & w 15.1%). The total nitration time was 1 hour at about -5°, and the yield was 54% of product contg 8.20% N. Although the product was carefully purified to be acid-free, it underwent decomp when allowed to stand for several days at RT (Ref 4)
Refs: 1) Bell - not found 2) G.T. Morgan & E.L. Holms, JCS 1932, 2670 3) G.T. Morgan et al., Chem&Ind 57, 887 (1938) 4) K.S. Warren, PATR 1103 (1941), p 2 and Table I

Methyl Pentanitrophenyl Nitramine (N-Nitro-N-methyl-2,3,4,5,6-pentanitroaniline, N-Methyl-N,2,3,4,5,6-hexanitroaniline).
(O$_2$N)$_5$N,C$_6$.N(NO$_2$)$_2$.CH$_3$, mw 377.17, N 26.00%, OB to CO$_2$ -14.85%, colorless cryst, mp 132° (evolves gas), detonates upon heating. Sol in chlf. Prep by nitration of a mixt of 3,5-dinitro-N-methylaniline & 3,5-dinitro-N,N-dimethylaniline. It is unstable and decomposes readily above
its mp or when boiled in w

Refs: 1) Beil 12, 772  2) J.J. Blanksma, Rec 21, 254 (1902)  3) Urbański 3 (1967), 65

2-METHYL-1,3-PROPANEDIOL AND ITS DERIVATIVES

2-Methyl-1,3-Propanediol (β-Methyltrimethylene glycol). \( \text{CH}_3\cdot\text{CH}2\cdot\text{OH}_2 \); mw 90.12; liq, bp 214–214.5° at 771mm and 110–111° at 14.5mm, d 1.0297g/cc at 0/0°. Can be prep'd by heating, on a w bath, methyltrimethylenebromide \( \text{CH}_3\cdot\text{Br} \cdot\text{CH}2\cdot\text{CH}_3\cdot\text{Br} \) with \( \text{AcOH} \), and saponifying the resulting dicetate with aq Ba hydroxide. It forms nitro derivatives

Refs: 1) Beil 1, 480 & [547]  2) A. Faworsky & N. Sokownik, Ann 354, 366 (1907)

2-Methyl nitropropanediol (2-Nitro-2-methyl-1,3-propanediol). \( \text{CH}_3\cdot\text{C(NO}_2\cdot\text{CH}_2\cdot\text{OH}_2 \); mw 135.12, N 10.37%; monocl crystals; mp 149–51°; bp decmpn. Sol in w (80p in 100p at 20°) and in alc. Can be prep'd by treating a mixt of nitroethane and formaldehyde in w with a small amt of K bicarbonate as catalyst. On nitration, it yields an expl, 2-Methyl-2-nitro-1,3-propanediol dinitrate (see below)


2-Methyl-2-Nitro-1,3-Propanediol Dinitrate (Nitromethylpropanediol dinitrate).
\( \text{CH}_3\cdot\text{C(NO}_2\cdot\text{H}_2\cdot\text{NO}_2\cdot\text{H}_2\cdot\text{SO}_4 \); mw 225.12, N 18.67%; OB to \( \text{CO}_2 \) –24.9%; waxy crystals; mp 37.4°; bp decmpn at 200° within 5secs. Sl sol in w, sol in alc, acet, eth and petr eth. Prep’d by gradually sifting 50g of dry, ground 2-methyl nitropropanediol into a mixt of 300g of 4:6 \( \text{HNO}_3\cdot\text{H}_2\cdot\text{SO}_4 \) with mechanical agitation at a temp of about 15°. After the addition, the temp was allowed to rise to 20° and kept there for ½ hour with agitation. After allowing the mixt to stand for 1 hour, it was transferred to a separatory funnel and the spent acid drawn off. The residual oil was washed twice with warm aq Na sulfite soln, and then with warm w until neutral to litmus. After drying under vacuum at 50°, the oil was chilled until it became milky in appearance and waxy crystals sepd (Aaronson, Ref 5, obtained a 76% yield). An addnl amt of material was obtained when a mixt of the washings and the spent acid was extrd with eth. The extr was washed with w, the eth evapd and the residue, after drying, gave an addnl yield of 16.2% for a total of 92.2% (Ref 5, p 7)

Methyl nitropropanediol dinitrate is nearly as powerful an expl as TNT, but more brisant, comparable to Tetryl. It was prep’d during WWII on a lab scale in Ger, and examined from the point of view of its gelatinizing properties on NC. Such properties were found to be rather poor, although its volatility, stability, etc were satisfactory (Ref 4)

The compound was also prep’d and examined in the USA by Picatinny Arsenal, Hercules Powder Co and others, and was found to have the following characteristics:

Brisance. 53g of sand crushed in Sand Bomb Test vs 48g for TNT (110.5% of TNT)

Explosion Temperature. Ignited above 240°

Heat of Combustion. Q 531.4kcal/mole

Impact Sensitivity. 1cm with BurMines app with 2kg wt (less sensitive than NG)

Power. About 135% of TNT in BallMort Test; about 160% of TNT in Trauzl Lead Block Test

Rifle Bullet Test. High order detonations

Thermal Stability. 9 to 30 minutes in 82.2° KI test, comparable to NG; and in 15–30 minutes in 135° Heat Test; no explosion in 300 minutes

Toxicity. Similar to NG

Uses. This substance, as well as other aliphatic compds such as nitroisobutylglycol dinitrate, comprising a branched chain hydrocarbon to which one nitro and two nitrate groups are attached, has been proposed by Bergeim (Ref 2) for use in commercial explos as a partial substitute for NG

Methyl Tetryl or 2,4,6-Trinitrotolyl-3-Methyl-nitramine. (2,4,6-trinitro-3-methyl-nitraminotoluene or methyl-[2,4,6-trinitro-3-methyl-phenyl]-nitramine). \( \text{CH}_3\text{C}_6\text{H}(\text{NO}_2)\text{3}_3\text{N} (\text{CH}_3)\text{NO}_2 \), mw 301.08, N 23.25%, OB to \( \text{CO}_2 \) -61.1%, mp 101 - 02\(^\circ\)C, bp expl. Colorless to yellow crystals from alc; sl sol in hot w, sol in bz, acet, chif & hot alc; sl sol in ligroin. Was first prepd by Rombough (Ref 2) in 1884 by nitrination of dimethyl-m-toluuidine with mixed nitric-sulfuric acid. Blankensma (Ref 3) prepd it in 1902 by nitration of 2,4,6-trinitromethylaminotoluene and detd its structure.

Davis (Ref 4) suggested preparing it from beta-and gamma-TNT's removed from crude TNT on purification with Na sulfite soln. The bulk of these impurities contain Na sulfonates of DNT's, and, if treated with methyamine, the following reaction occurs:

The resulting N-methyldinitrotoluidines, when further nitrated, yield methyl Tetryl. Methyl Tetryl is a less powerful expl than Tetryl, and has not been used commercially.


Note: See also under 2,4,6-Trinitro-3-methyl-nitraminotoluene in Vol 5, D1375-L & R

**METHYL TRIMETHYLOLMETHANE AND DERIVATIVES**

*Methyl Trimethylol Methane* (Trimethylolmethane, Pentaglycerol or Trimethylol ethane). \( \text{CH}_3\text{C}(\text{CH}_2\text{OH})_3 \), mw 120.17, OB to \( \text{CO}_2 \) -173.09%, white cryst, mp 199\(^\circ\)C, bp 135 - 37\(^\circ\) at 15mm, sol in dioxane, w & alc (Refs 1, 2 & 4). Prepn from propionaldehyde & formalin condensation in cold aq soln using lime; 62% yield (Refs 2 & 3)

Refs: 1) Bell 1, 520 & (2348) 2) Blatt, OSRD 2014 (1944) 3) Blomquist, OSRD 4134 (1944) 4) Sax (1968), 1199
Methyl Trimethylnitramine Methane. (Pentaglyceryl Trinitramine, PGX).
CH₃C(CH₂HNNO₂)₃, mw 252.23, N 33.33%,
OB to CO₂ -63.43%, white cryst, mp 130°-31°
decomps; sol in ethyl acetate & nitromethane.
Prepn from pentaglyceryltriurethane by nitrata-
ion with a mix of acetic anhydride & 98% nitric acid at 0-5°. Expln temp is 335°
(ignition). Internation heat test at 75° shows
0.0% loss. Power using ballistic mortar is
111.8 (TNT=100). Sensitivity to initiation
30cm at the 50% point. Stability at 135°;
ignition in 10mins. Vacuum stability at 100°
is 12cc in 25 hours
Refs: 1) Beil - not found 2) Blomquist,
OSRD 4134 (1944)

Methyl Trimethylnitramine Methane, Silver Salt
(Silver Pentaglyceryl Trinitramine).
CH₃C(CH₂NAgNO₂)₃, mw 572.81, N 14.68%.
OB to CO₂ -23.74%, sol in aq ammonia.
Prepn from pentaglyceryltrimineurethane in ammno-
acal soln upon addition of Ag nitrate in acetic
 acid. The Ag salt detonates when heated
Refs: 1) Beil - not found 2) Blomquist,
OSRD 4134 (1944)

Methyl Trimethyl Methane Trinitrate (Tri-
 methylol methyl methane trinitrate, 1,1,1-
 Trimethylene trinitrate, Nitropentagly-
cerin, or Metrol [trinitrate]).
CH₃C(CH₂ONO₂)₃, mw 255.17, N 16.47%.
OB to CO₂ -34.50%, colorless, oily liq, mp
9°, fr p 7.5°, d 1.46g/cc at 22°/4°, RI 1.4760
at 22° (Refs 2 & 3). Prepn from methyl
trimethylmethane by nitrataion using mixed
acid (HNO₃/H₂SO₄) at 20° followed by
pouring on cracked ice; yield is 81% (Refs 2
& 3). Qc is 674cal/mole. Heat test at 135°
is acid in 35 min; no expln in 300 min (Ref
2). Hygroscopicity at 25° shows a gain of
0.07% weight at 90% relative humidity and
0.14% at 100% RH. Impact sensitivity: Fl of
74% relative to PA, positive at 16.7cm vs
35-45cm for TNT; 1kg weight negative at
66cm (Ref 2). Power as shown by ballistic
mortar, is 136% of TNT, and by lead block
expansion is 139% of PA. Stability at high
temp is indicated by ignition at 235° with
expln at 360°. Vacuum stability at 100° is
11.3cm/5g in 48 hours (Ref 2). See also under
Metriol and its Derivatives in this Vol
Refs: 1) Beil - not found 2) Blatt, OSRD
2014 (1944) 3) Blomquist, OSRD 4134
(1944)

1,1,1-Trimethylol-2-Chlorethane Trinitrate
(Pentaerythritol monochlorohydrin trinitrate).
ClCH₂C(CH₂ONO₂)₃, mw 289.61, N 14.51%.
OB to CO₂ -27.62%, mp 43°-50° (Ref 3)
Prepn from pentaerythritol monochlorohydrin
by nitrataion which produces a mix of the di-
& tri-nitrate (Ref 2). Impact sensitivity using
a 2kg wt at 170cm shows no explns vs 35cm
for PA (Ref 3). Power from lead block expa-
nsion is 305cc vs 285cc for TNT (Ref 3)
Refs: 1) Beil - not found 2) Westfälisch-
Anhalt, SS-A-G, GenP 638432 (Nov 14, 1936)
& CA 31, 1212 (1937) 3) Blatt, OSRD
2014 (1944)

2-Methyl-2,4,4-Trimethylpentane-1,3,5-Triole
Hexenitrat e (Ennahexite hexenitrate).
(O₂NOCH₂)₃CCNOONO₂C(CH₂ONO₂)₂CH₃,
mw 494.29, N 17.01%, OB to CO₂ -22.70%,
mp 74°-75°. Prepn from nitrataion of the con-
densation product formed with methyl ethyl
ketone and formaldehyde. Impact sensitivity
is 50% positive using a 2 pound wt dropped
18 inches
Refs: 1) Beil - not found 2) Blatt, OSRD
2014 (1944)

2-Methyl-2,3,3-Trinitrobutane.
(CH₃)₂C(NO₂)₃.C(NO₂)₂.CH₃, mw 207.17.
N 20.29%, OB to CO₂ -65.65%, white prisms,
mp 190°, explodes. Readily sol in organic
solvents. Prepn by gently refluxing bis-tri-
methylethenenitroschloreidene with concd
nitric acid (d 1.42g/cc) (Ref 1 & 3). Qc
700.46kcal/mole (Ref 4). Impact sensitivity
is less than TNT (Ref 2). Power by ballis-
tic mortar is 106% of TNT (Ref 2)
Refs: 1) Beil 1, 141 2) Anon, BurMines,
High Explos Res Div, TR No 25 (1942)
3) Blatt, OSRD 2014 (1944) 4) A.J. Miller
CA 39, 1352 (1954)
Methyl Violet Tests (Storage, 120° or 134.5° Heat Tests). Propellent stability tests using special 0.1 or 1.0N methyl violet paper. See under German 135° Stability Test in Vol 6, G70-L to G71-L, and Methyl Violet Paper Test (below) Prepn of 0.1N Paper. Weigh into a casserole, 0.2500g of methyl-p-rosaniline (basic compd). Add an excess of glacial acetic acid, and evap to dryness on a steam bath. This will yield about 0.3g of rosaniline acetate. Rinse into a 1L volumetric flask, using a total of 300ml of distd w. Add exactly 40ml of c.p. glycerin and 0.1680g of methyl violet NE (duPont Co), or methyl violet 2B (National Aniline & Chem Co), or crystal violet. Make up to 1L with 95% alc and mix well. Transfer a small quantity of the soln into a rectangular glass or stainless steel trough (about 16"x6"x10" deep), which is located in a room free of acid fumes. Raise one end of the tray so that it will be in a tilted position. Cut Schleicher & Schull filter paper No 597 sheets, 58x58cm, into four parts. Hold one edge of the paper by means of two clips, dip it into the trough up to the upper edge, and then draw the paper slowly (in about 5 seconds) thru the soln and up and over the side of the trough in order to remove the excess liq from the paper. Hold the paper in a vertical position over the tray until the liq starts to drip, then grasp the bottom edge by use of two clips. Wave the strip gently to and fro for about 30 seconds in order to evap the alc. Fasten the strips with metal push pins to wooden blocks and allow to dry overnight in a dark room, free from acid fumes. Trim the edges and cut the paper into strips 20x70cm or 20x140cm and store in a well-stoppered bottle.

After seasoning for about a week, compare the new paper with standard 0.1N methyl violet paper by dropping strips of each into a container with unstable propellent (one which will give a surveillance test of about 30 days at 65.5°). Both papers should show the same degree of discoloration after a given time period Prepn of 1.0N Paper. Weigh out 2.5g of basic p-rosaniline and evap to dryness (as above) with an excess of glacial acetic acid. Rinse into a 1L volumetric flask, using a total of 300ml of distd w. Add 40ml of c.p. glycerin, 1.68g of methyl violet, and make up to 1L with 95% alc. Dip and dry the paper in the same manner as the 0.1N prepn. After the paper has been seasoned for about a week, trim the edges and cut into 20x70cm strips. Compare with standard 1.0N methyl violet paper in the German 134.5° Stability Test (see Vol 6, G70-L) using both pyrocellulose and propellent. In a 30 minute test the results obtained should not differ by more than ±1 minute using different lots of paper. On being exposed to nitric oxide fumes, these papers slowly turn green, followed by a salmon pink coloration Methyl Violet Paper Test (Field Test for Propellent Powders). This method of testing propellents using 0.1N methyl violet paper directly in the containers in which the powder is stored, was developed at Picatinny Arsenal in 1928–29 (Refs 1 & 2), and was adopted by the Ordnance Dept to replace the "Observation Test" about 1931 [Note: The "Observation Test" was intended to detect the initial decomp of propellent, and was conducted at all depots and posts where powder was stored. A 6oz sample of each lot of powder with a strip of methyl violet test paper was placed in a glass-stoppered bottle, with the paper not in contact with the powder. The test was conducted in the magazine in which the propellent under test was stored. Bleaching of the test paper was taken as an indication that the powder had started to de-
teriorate. The test was run continuously and new samples were selected each year. Test papers which lost color gradually could remain in their bottles until they were completely bleached, but papers which showed a marked color change were replaced every two months. A report was made of any evidence of deterioration, and special stability tests were run on the lot in question (Ref 3).

The Methyl Violet Paper Test was originally developed for the purpose of testing the stability of pyro powders in bulk storage, and was later extended to other powders. The test is particularly useful in cases where the propellant is hygroscopic (such as pyro) and decomps more rapidly, at the same temp, in the presence of moisture than when dry. If, in testing one lot of propellant stored in several containers, some of them show instability, the indication is that such containers have developed leaks and that moisture has penetrated to the powder.

Although moisture affects nonhygroscopic single-base propellants very little, and leaky containers do not have the same significance with respect to hazard in storage as in the case of pyro powders, the Methyl Violet Paper Test is considered useful because the paper will undergo a color change in the event the propellant becomes unstable.

**Test Procedure.** Suspend in each bulk powder or propellant charge container, in the atm above the powder, one strip of \(\frac{3}{4}\)" x \(\frac{3}{16}\)" 0.1N methyl violet paper. To do this, clamp one end of the paper between the lid and the container. In handling the strips of test paper, great care should be taken to insure that they are not contaminated with dirt or perspiration from the hands. Examine the cover gasket, and if it is defective, replace it with a new one. Allow the containers to remain in the storage magazine at the desired temp (if the powder is intended for use in tropical countries, a temp of 50° is suitable), and examine the test paper periodically. The methyl violet test paper color is categorized as Class 1 (original violet color), Class 2 (any intermediate color between the original violet and white or pale yellow) or Class 3 (white, or beyond to a pale yellow, in which case the paper becomes brittle).

If the propellant is single-base, and there is no reason to suspect that it is unstable, the paper should not change color after exposure for one year. In this case, at the end of one year, the strip of test paper is removed, replaced by a new one, and the test continued.

Where definite loss of color by bleaching is noted, the content and container should be inspected to determine the cause. If correctable, such as a faulty gasket, broken container, etc., the gasket is changed or the powder is transferred to another container. A new strip of test paper is inserted and the propellant replaced in storage with the container definitely marked to insure reinspection at the end of one year. If the defect cannot be corrected, as in the case of deteriorated propellant, the propellant is destroyed or otherwise disposed of.

In cases where a lot of propellant has successfully passed the one-year exposure to methyl violet paper, only a 3% inspection of the exposed test strips need to be made thereafter until such inspection indicates progressive deterioration of the propellant or other nonstandard condition, at which time 100% inspection and test of the lot under suspicion will be resumed.

It is considered desirable that succeeding annual inspections include at least 1/3 of the containers included in the original 3% inspection as outlined above. In this manner, such containers may be considered as a basic comparative control with reference to the balance of the lot under test.

If the propellant is double-base, it has been observed that even the most stable propellants bleach methyl violet paper in much shorter periods than one year. Investigations conducted by P.F. Macy at Picatinny Arsenal (Ref 4) showed that diphenylamine-stabilized double-base propellants in service storage at about 30°, may be considered of satisfactory stability if they do not cause complete bleaching of 0.1N methyl violet paper in one month or less. Such propellants always show satisfactory stability when subjected to the 65.5° Surveillance Test. It was observed at the same time, that double-base propellants which had deteriorated, but were not yet hazardous, took from 11 to 24 days to bleach methyl violet paper at 30°.

Later tests at Picatinny Arsenal revealed that methyl violet paper very often faded in shorter time periods than described above, even for perfectly stable powders, as detd by the 65.5°
Surveillance Test and the 134.5° Heat Test. This applied particularly to double-base propellants, although some single-base propellants also gave erratic results. For these reasons, work was undertaken at Picatinny Arsenal to find an indicator that would be more reliable than methyl violet. About 60 commercially available dyes were examined by S. Helf (Ref 5) in exptl indicator paper tests, of which only three were found to be superior to methyl violet: benzoazurine, trypan red and ethyl violet. Laboratory and surveillance testing showed that papers prepd with a 0.1% soln of benzoazurine did not change in color after one year when used with stable double-base propln, while methyl violet paper was bleached in nearly every case. The other two indicators mentioned above, trypan red and ethyl violet, were not as satisfactory as benzoazurine, although they were better than methyl violet. On the other hand, when paper strips with benzoazurine, trypan red or ethyl violet were exposed to unstable double-base propln, or to nitrogen oxide fumes, prepns in the lab, all of the papers either bleached or faded, as did the methyl violet paper.

Following are methods of prepns as well as the original colors and changes of coloration of the indicator papers:

**0.1% Benzoazurine Paper.** Dye soln, prepnd by dissolving 2g of the product, supplied by Hartman-Leddon Co., in 1900ml of w and 100ml of glycerin; Blush-violet → Light violet → Bleached

**0.1% Trypan Red Paper.** Prepnd as above from product supplied by the Allied Chemical & Dye Corp; Rose-red → Light violet → Bleached

**0.1% Ethyl Violet Paper.** Prepnd as above from product supplied by National Aniline & Dye Co; Medium violet → Blue → Bleached

As of this date, the use of the new test papers has not been standardized.

**Written by S. M. KAYE**

**Refs:**
1) W.T. Ingraham, PATR R40 (1928)

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**METRIOL AND ITS DERIVATIVES**

**Metriol** (Pentaglycerol, 2-(Hydroxymethyl)-2-methyl-1,3-propanediol, Methytrimethylethylene). H₃C.C(CH₂OH)₃; mw 120.15; white needles from abs alc; mp 195° (sublimes without decompn). Was first prepd by Hosaeus (Ref 2) by condensing formaldehyde and propionic aldehyde in cold aq soln in the presence of lime. Metriol is v sol in w, alc and acet ac; is insol in eth. It may be nitratd to an expl trinitrate, and acetylated to a nonexpl triacetate

**Refs:**
1) Beil 1, 520 2) H. Hosaeus, Ann 276, 76 (1893)

**Metriol Trinitrate** (MTN, 1,1,1-Trimethylethylene trinitrate, Nitropentaglycerin, Metriolato Italian). H₃C.C(CH₂ONO)₃; mw 255.15, N 16.47%, OB to CO₂ -34.5%; oily, slightly turbid liq, mp -3°, bp decompn beginning at 182°, d 1.47g/cc at 22°, RI 1.4752 at 25°.

According to Italian sources, it was first prepd and patented by the Bombrini-Parodi-Delfino Co of Italy under the name "Metriolo". A Ger patent of 1927 (Ref 1) also describes the prepns and gives some properties. It states that the trinitrate is a viscous expl oil which remains liq at -15°, is more stable than NG, and can be worked up into powdered or gelatious products in the same way as NG. The compound was also known in France before WWII under the name "Nitropentaglycerin" and Buriot and Thomas (Ref 2) detd its heat of combustion. The Germans learned about "Metriolo" before WWII, and, recognizing its merits as a flash and erosion-reducing agent, started to manuf it. The method employed by I.G. Farbenindustries AG was as follows (Ref 6):

In the pilot plant procedure, 50kg of finely powdered metriol was fed thrn an endless screw (dosiernschnecke) to a nitrator provided with cooling coils and an agitator, contg 175kg of mixed acid (65/35 nitric-sulfuric). The nitration time was about 20 minutes at 20°. The mass was allowed to settle for 15 minutes, and the oil separated from the spent acid in the same manner as in the manuf of NG. The sepd oil was washed, first with w at 40°, then with aq soda soln, also at 40°, and finally with w. The yield was about 100kg of oil contg 16.32 to 16.36% N. In Italy, yields as high as
93% of theoretical were claimed

On a lab scale, metriol is nitrated by carefully mixing it with 3.5p of 65/35 nitric-sulfuric acid maintained at 20°, stirring for 30 minutes, cooling to 5°, and pouring the reaction mixt on ice. It is extd with eth, w-washed, and adjusted to pH 7 by shaking with a Na bicarbonate soln and again w-washed three times. It is then dried with Ca chloride, filtered, and freed of eth by bubbling with dry air until minimal rate of loss in weight is attained. The yield is 88% of the theoretical, and the product has a nitrate-N content of 16.35% (calcd 16.47%). The RI at 25° is 1.4752 (Ref 10)

MTN is practically insol in w (<0.015g/100g at 25° and <0.015g/100g at 60°); sol in alc and other organic solvents

It is a powerful expl, as sensitive to impact as NG (BurMines drop test with 2kg wt, 4cm). Its Abel Test stability is about 20 minutes at 82°. MTN alone does not gelatinize NC unless the temp is raised to 110°, which would be dangerous, but if mixed with only 8% of the triacetate, it gelatinizes the NC at 80°

Physical and chemical properties of MTN, detd primarily at Picatinny Arsenal, are as follows:

Brisance (Sand Test). 43.7g vs 48.0g of TNT, or 91% or TNT

Explosion Temperature. 5 secs at 235°

Friction Pendulum Test. Explodes with steel and fiber shoes

Heat of Combustion. 2642cal/g at C & water liq, or 674cal/mole

Heat of Formation. 422cal/g at C & 446 cal/g at C (Ref 9)

Hydrolysis, % Acid. 10 days at 24°, 0.018; 5 days at 60°, 0.115

Hygroscopicity, %. At 25°, gains 0.07 at 90% RH and 0.14% at 100% RH

Impact Sensitivity. BurMines app, 2kg wt, 4cm; PicArsn app, 20°

Power. Trauzl Test, 140% of TNT; Ballistic Mortar, 136% of TNT

Stability. In 100° Heat Test loses 2.5% wt in first 48 hours and 1.8% in second 48 hours; no expl in 100 hours. In 100° Vacuum Stability Test, evolves 1.9ec of gas per g in 40 hours; not considered very satisfactory

Volatility. At 60°, loses 24mgs/cm² in 1 hour

MTN was used as a flash and erosion reducing additive in propelts (Refs 7 & 8), and as an ingredient of commercial expls

Refs: See under Metriol Triacetate (below)

**Metriol Triacetate (MTA, Acetometriolo in Italian). H₃C.C(CH₂.OO.CCH₃)₂, mw 246.25.**

Was prep'd by Bombini-Parodi-Delfino Co in Italy, and then by I.G. Farbenindustrie AG in Ger by azeotropic distn of acet ac and methyltrimethylmethane in benz (Ref 2, p 4)

The Germans found it to be a good gelatinizer for NC, but possessing no stabilizing action. The Italians found that the addition of as little as 8% MTA to Metriol Trinitrate (MTN) improved the gelatinizing properties of the latter (see under Metriol Trinitrate). Its Q₇ is 1347cal/g, and Q₉ is 1376cal/g (Ref 9)

The following propelts cntg both MTN and MTA were manufd in Italy (Ref 3, p 7):

**M4;** NC 55.0, MTN 40.5, MTA 2.0 & Centralite 2.5%

**M6;** NC 57.5, MTN 36.0, MTA 4.5 & Centralite 2.0%

**M8;** NC 59.0, MTN 33.0, MTA 5.5 & Centralite 2.5%

**M10;** NC 59.0, MTN 29.5, MTA 7.0, Centralite 3.5 & vaseline 1.0%


9) P. Tavernier, MP 38, 302 & 328 (1956)
Mettogang Recorder. A device, designed by Mettegang in 1904, for measuring the vel of deton of expls with an accuracy of ±10 to 15 meters per second. The apparatus consists essentially of a strong, well-turned and balanced, heavy cylinder of steel which is rotated at a high but exactly known vel. The vel of its smoked surface relative to a Pt point which almost touches it may be as much as 100m/s. The expl to be tested is loaded into a cylindrical steel cartridge from 1 to 4m in length. At a known distance apart, two thin copper wires are passed thru the expl at right angles to the axis of the cartridge. If the expl has been cast, the wires are bound tightly to its surface. Each of the wires is part of a closed circuit thru an inductance, so arranged that, when the circuit is broken, a spark passes between the Pt point and the steel drum of the chronograph. The spark makes a mark upon the smoked surface. When the expl is fired by means of a detonator at one end of the cartridge, first one and then the other of the two wires is broken by the detonating expl, and two marks are made on the rotating drum. The distance between these marks is measured with a micrometer microscope with a vernier reading to 0.01mm, making it possible to det the time interval to within 1x10^-7 second when the drum vel is 100m/s. The time duration which corresponds to the movement of the surface of the rotating drum thru this distance is calcld, and this is the time which was required for the deton of the column of known length of expl which lay between the two wires. From this, the vel of deton in m/s is computed


M.G.C. Abbreviation for “Military Gun Cotton”, which is NC between about 13.0–13.5 N content. It is used in various propnts

Mica. A class of silicates of a wide variety of compns, but consisting essentially of silicates of Al (sometimes partly replaced by Fe, Cr, etc) and an alkali, such as K, Na or Li. All characteristically cleave into thin sheets, which are flexible and elastic. Occurs naturally thru-out the world. In its powd form, it has been used in pyrotechnic compns (Ref 1), as well as in Dynamite

Refs: 1) Davis (1943), 95 2) CondChemDict (1971), 586-L

Mica Dynamite or Mica Blasting Powder. An expl invented by G. Mowbray in the USA in 1873, and used in the latter part of the construction of the Hoosac tunnel, replacing the guhr Dynamite used in the beginning. It consisted of 48 to 60p of finely powd mica, thoroughly blended with 52 to 40p of NG. Because of the fact that NG was not absorbed by mica but adhered to the scales, thus resulting in a large exposed surface area, the resulting Dynamite was more sensitive to deton than guhr Dynamite (Ref 2). The max amt of NG that could be held by mica was 52% vs 75% for guhr

Berthelot (Refs 1, 2 & 5) detd vel of deton of mica and guhr Dynamites, and found that the former gave slightly higher values with the same NG content. He attributed this to the cryst structure of mica, which made it less deformable than the amorphous silica kiesel-guhr. General Abbott (Ref 2) found the expl effect of 52% mica Dynamite under w was about 83% that of guhr Dynamite congl 75% NG. According to Barnett (Ref 3), mica Dynamites were also used in Spain, where they contd about 42% NG

Michailovsky (Mikhailovsky) Powder. A mining expl resembling tea in appearance. Contains K chlorate 50, sawdust and/or powd tanbark, bran, etc 45, and Mn dioxide 5%. It was also called "Poudre des Mineurs".
Ref: Daniel (1902), 439 & 441

own reaction products; and all three approaches have been explored for high energy propellant ingredients. In the aqueous coacervation process, a film-forming colloid dissolved in water is pptd into a second, concd, colloid-rich, aq phase which collects on and adheres to the surface of suspended particles or droplets to form a continuous shell. The shell is hardened and cured by appropriate cooling and/or chemical treatments, after which the capsules can be filtered off and collected as a dry powder (Refs 5, 7 & 11). A few of the polymer wall materials which can be deposited by this process are gelatin, polyvinyl alcohol, methyl cellulose, gum arabic, carboxymethyl cellulose and starches. The material to be encapsulated must of course be insoluble in and unreactive with w. Precipitation is similar in that the capsule wall former is dissolved in a solvent and deposited onto the suspended particles or droplets—by no means being done. At the interface between the solvent and particles is another major non-solvent (Refs 2, 4 & 11). Organic solvents are most commonly used, and encapsulating polymers include ethylcellulose, NC, polyvinylidene chloride, polystyrene, polycarbonate, polymethylmethacrylate, polyvinyl acetate and others. Interfacial polymerization produces a polymer such as nylon at the interface between the layers of two precursor materials such as (in the case of a nylon) a diamine and a diacid (Refs 3 & 11). If the particle or droplet to be encapsulated is made to pass thru the interface by, say, sedimentation, it will pick up a coating of the polymer as it passes thru.

Polymer films can also be deposited on solid particles by vapor phase reaction or from a melt. The best example of vapor phase reaction is the deposition of Union Carbide's "Parylene", a derivative of p-xylene. In this process, dip-xylene, or more commonly a halogenated derivative of it, is vaporized in a vac and thermally dissociated into the very reactive monomer, a diradical. The monomer is allowed to condense on the surface of the particles to be coated, where it instantaneously polymerizes to form a high molecular weight, polymeric film (Ref 10). Less reactive, vaporizable or meltable polymers can be applied by hot spraying onto agitated particulates or by deposition in a fluidized bed or in liq suspension (Ref 2). Wax is a common example of wall material applied in all three ways.

Metal capsule walls are most commonly deposited onto particulates by vac evaporation of, say, Al onto an agitated bed of particles to be coated (Ref 2). Any metal which can be evaporated in a bell jar can be used. Metals can also be deposited from soln by reduction from ions. Examples are Ag and complex Ni phosphides in electroless processes.

A final category of encapsulating materials consists of reaction products of the nucleus material and a reagent. For example, pellets of nitronium perchlorate have been encapsulated in shells of the less reactive ammonium perchlorate (AP) by exposing the pellets to ammonia gas. The fragile AP shells were usually further protected by a top-coating of Al or a polymer film (Ref 2). The most familiar example of this process is the natural one wherein Al powders (or articles) become coated with a protective coating of Al oxide thru exposure to atmospheric air.

Microencapsulation is usually attempted because a proposed ingredient is too reactive or too sensitive to withstand exposure to other ingredients or to the environment. For example, the very energetic oxidizer nitronium perchlorate (NP) cannot be mixed directly into a propellant or expl formulation because of its extreme reactivity. It is actually a solid anhydride between nitric and perchloric acids, and even traces of moisture hydrolyze the surface layers to free concd nitric and perchloric acids. Moreover, it is so reactive that it will literally explode on contact with substances such as aromatic compounds including solid naphthalene. Consequently, the only real hope of using it lies in effective encapsulation; and extensive efforts have been made to encapsulate it. Processes involving w or organic solvents are obviously inapplicable, but small pellets have been successfully coated with Parylene and with AP and Al (Refs 2 & 10). The efforts were not fully successful, though; because it never was possible to form capsule walls thick enough to protect the NP completely and at the same time thin enough not to add too much inert material to the formulation.

The US Air Force has studied the encapsulation of liq monoproplnts such as alkyl nitrates in polymer films to form small spheres much like ball powder for use as gun proplots (Refs 6, 8 & 9). Suspension coating techniques were used, and microcapsules were made with gelatin,
NC, polyvinyl alcohol and combinations thereof. A free-flowing "ball powder" containing 60-80 wt percent of liq monopropellant was obtained and successfully fired in small arms cartridges. There were serious difficulties with permeation of the volatile liquids thru the capsule walls and with ignition of the smaller capsules.

Most of the energetic materials related work on microencapsulation was done on the high-energy rocket propellent program around 1960 to 1970 and was classified CONFIDENTIAL or SECRET at the time. Most of the work is now declassified. The refs contain several good reviews of the state of the art, both military and general.

Written by J. BROWN


Micrograin. A dust-like mixt of Zn and S used as an unrestricted burning rocket propellent. It has a linear burning rate of 60.1 inches/sec as compared to 1.1 inches/sec for ballistite, and costs $0.20/lb vs $5–10 for ballistite. The sp impulse of micrograin is approx 50 sec, that of ballistite is 200 sec. 
Ref: G.S. James, Astro-Jet 1948, No 21, 2-12 & CA 44, 5591-92 (1950)

Microscopy. A broad definition of microscopy is the observation and measurement of optical parameters with any instrument that uses energy sources such as photons, electrons or X-rays to provide an enlarged image of an object. Energetic material parameters that have been observed and measured include quantity, size, shape and color (Expts: Refs 12-15, 19, 20, 25, 25a, 27, 28, 32, 48 & 62; Propints: Refs 1-7, 11, 22, 23, 27 & 40; Pyrots: Ref 40); qualitative identification, mp and crystal growth rate (Expts: Refs 13, 14, 26, 30, 34, 36, 38, 41 & 53); and combustion parameters such as burning rate, flame erosion of metals and component behavior (Expts: Refs 9, 10, 16, 17, 34, 35, 39, 40, 46, 47, 49 & 52; Propints: Refs 8, 37, 40 & 56; Pyrots: Ref 40)

The optical microscope (OM), which has
always been of use from the crude lenses of the ancient Assyrians, thru advances made in optics and OM design by Kepler, Tortona, Martin, Adams and Young, to the latest Balpan or Zeiss creations for crystal morphology, has found important application in energetic materials' research (Refs 51, 61 & 62). This importance is evidenced by work which has ranged from the crystal habits or morphology of expls (Refs 12-15, 26, 30 & 41) and proplnts (Refs 1-7 & 11), to expl and proplnt particle sizing and counting (Refs 19, 20, 27, 28, 32, 48 & 63), to metallographic investigations (Refs 8 & 16).

Many attachments and special devices have been developed to extend and implement the applicability of the OM. One of these is a controlled atmosphere microscope dry-box which offers reproducible environmental control for applications involving toxic, air, or moisture sensitive ingredients, typical of many energetic materials (Ref 33).

Procedures for OM particle sizing and counting of expls are presented in Refs 19, 20, 32, 48 & 63. A procedure for proplnts is presented by J.W. French (Ref 27), who used both OM and EM (electron microscopy) to study plastisol NC curing. He found that the cure time of plastisol NC is a logarithmic function of temp, and direct functions of chemical compn and total available surface area, as well as of particle size distribution. It should be noted that extensive use of statistics is required as a time-saving means of interpreting particle size distribution data. The current state-of-the-art utilizes computer techniques to perform this function, and in addition, to obtain crystal morphology data (Ref 62).

The epochal advances in energetic material OM made in 1944 by the OSRD committee headed by A.T. Blomquist provided a cohesive guide for quantitatively identifying primer and detonator ingredients and formulations. The technique involves using the individual morphology of a composition's constituency, as well as thru the application of specific color-resulting chemical reactions. Individual energetic materials, inorganic and organic additives so identified included MF (Mercury Fulminate), LA (Lead Azide), Pb Styphnate, Pb Picrate, Pb 2-4 di-nitroresorcinol, Pb 4-6 dinitroresorcinol, Pb thiocyanate, Pb nitrate, Pb chromate, Pb oxide, Red Pb, K chloride, Sb sulfide, K nitrate, Ba nitrate, Diazadinitrophenol, Tetracene, S, Ca silicide, Si, sand, glass, Si carbide, C, gums, PETN, Tetryl, TNT, RDX, etc (Ref 13).

A work of equal magnitude, again by Blomquist (Ref 14), is directed toward the OM examination of high expls and boosters. It explains comprehensively how to identify these components using fusion analysis, optical crystallography and polymorphism. Materials so characterized include Amm nitrate, Amm picrate, Ba nitrate, Pb nitrate, DINA (Diethanol-nitramine dinitrate), DNT (Dinitrotoluene), EDDN (Ethylene diaminedinitrate), HMX, PETN, RDX, TNT, TNB (Trinitrobenzene), various waxes, etc. Procedures are also included for the microscopic identification of mixts, and the particular manufg process used to form the mixt, i.e., plasticized, pressed or cast. The importance of the methodology presented, aside from the universality of the technique, lies in the use of microgram samples, and in many instances, the non-destructivity of the procedures employed.

OM was used in a basic NC study by S.I. Morrow of PicArsn (Ref 56). He used glass capillary tubes to observe the combustion of thin films of NC (12.6% N) at high press (He at 26-34atms) while heating at the rate of 10° per min. It was found that the NC tended to deflagrate in a manner suggestive of ignition caused by the presence of N oxides. Older NC films behaved differently from freshly prepared specimens in that pyrolytic degradation occurred at higher temps.

One of the more important uses of OM is the study of crystallization growth rates. K. Cermak constructed an interference microscope with which measurements can be taken to 50° (Ref 31). This app allows for study of the decompn of the solution concentrated in close proximity to the growing crystal of material such as Amm nitrate or K chloride. In connection with this technique, Stein and Powers (Ref 30) derived equations for growth rate data which allow for correct prediction of the effects of surface nucleation, surface truncation in thin films, and truncation by neighboring spherulites.

In order to obtain higher magnification than is possible with light microscopy, by a ratio of 1000 to 1, instruments employing magnetically
deflected electron beams were devised, and were called electron microscopes (EM). For a short, historical survey of EM’s, see Vol 5, E73-L to E77-L. A large amount of work has been conducted on energetic materials using two basic types of EM’s, the transmission electron microscope (TEM) (Refs 17, 18, 21–25, 27, 29, 34, 35, 43, 45, 54, 58, 60 & 62), and the scanning electron microscope (SEM) (Refs 36, 37, 39, 40, 42, 43, 44, 45, 46, 47, 49, 50, 52, 53, 55, 59, 60 & 62).

A comparison of these two magnification systems is important. The internal structure of energetic materials is revealed using the broad, fixed beam of the TEM so that internal stresses can be determined (Refs 17, 42, 58 & 62). The SEM, on the other hand, examines the surfaces of materials with its moving, narrow electron beam, which is reflected (Refs 40, 43, 49 & 62). The TEM is therefore especially useful for studying the effects of specimen exposure to heating, cooling, stress, etc., after the fact, while the SEM is excellent for surface examinations of corrosion or combustion phenomena taking place in situ. TEM works because electrons passing thru matter may be absorbed or scattered by various mechanisms, but the effects of interest in TEM involve, primarily, coherent elastic scattering or diffraction. This implies that the specimen to be studied must be crystalline, and that the facts deduced from its study are correlative information about the crystal structure and specific orientation of the specimen (Refs 43 & 45). Hence, specimens must satisfy certain conditions if they are to yield satisfactory images in the TEM: (1) they must be thin enough to transmit a large fraction of the incident electrons with only minor changes in velocity and direction, and (2) they must maintain their character in vacuum, and undergo the amount of electron bombardment essential for image formation without deterioration (Refs 45 & 62). Therefore, the class of objects which can be studied directly are large (crystalline) organic molecules, finely divided matter, or thin films. This means that surfaces of etched metallographic or other compact specimens must be investigated directly by observing thin film replicas. A replica is a means of reproducing the detail of a specimen surface on an amorphous, stable film. These replicate surfaces can also be fabricated from carbon which has been vacuum deposited on the specimen. The specimen is then dissolved or polished away. A two-step carbon replica can also be made from a plastic mold or copy of the original specimen. The preparation of replicas is discussed in Refs 17, 21–25, 29 & 35.

An important area of work utilizing TEM involves the study of metals and metal oxides. Explosively formed or fractured metals are of special interest using this technique (Refs 35 & 46), as are studies of metallic smoke particles (Ref 17) and metallic stress phenomena (Ref 34).

Another area of TEM application to energetic materials is the work of S.M. Kaye at PicArsn on exols and proplnts. He used TEM to establish a procedure for detg the particle size distribution of LÅ batches of different crystal habits from various manufacturers (Ref 25). He showed that the success or failure of ballistic testing of M-17 proplnt was related to the number and character of cracks and voids observed in the grain surface (Ref 22). In another study, Kaye found that a correlation existed between the type of surface active agent used in the manuf of M-15 proplnt and the successful dispersion of the crystalline ingredients (Ref 23). In an examination of M-8 mortar increment proplnt which had deteriorated in storage, he discovered bacterial infestation penetrating deeply into the grain structure, with resultant unacceptable ballistic performance. It was concluded that wash water used in the processing of this proplnt was contaminated (Refs 21 & 24).

As part of a basic study on M-8 proplnt, Revere (Ref 21), using TEM, discovered that proplnt stored at −20° and −40° for 12 hour periods became wrinkled and exhibited definite parallel cracking and changes in crystalline structure, which was reflected in erratic burning.

Although the SEM has about one-tenth the magnification of the TEM, it offers the advantage of being able to examine a specimen surface without resorting to replication. Specimen topography is represented in such excellent detail that the image produced gives the impression of being three dimensional (Refs 17, 18, 34, 35, 40, 43, 49 & 50).

A major investigative effort using SEM at the US Naval Weapons Center was concerned with solid proplnt combustion (Refs 37, 39 & 47).
The study was divided into three categories, the deflagration of single crystals of Amm perchlorate (AP), ignition of individual Al particles, and the burning of polyurethane type propellant containing AP, K perchlorate or HMX of varying particle sizes as oxidizers. Interpretation of SEM observations revealed that at pressures less than 2000psi, AP crystals deflagrate from a melt instead of by direct vaporization (sublimation); that the fragmentation of burning Al particles is caused by overpressurization within an Al oxide globule rather than by superheating of the globule itself. The propellant study determined that burning rate was inversely proportional to AP and HMX particle sizes and was slightly affected by K perchlorate particle size. It was also found that the reaction mechanism is diffusion-pressure flame controlled for AP propellants, and that K perchlorate propellant burns via a gas-phase chemical reaction of the second order. The HMX propellants melted in such a manner prior to burning that attempts to determine reaction mechanisms from reaction site observation was not possible.

Another SEM application is the work of Markham and Cox of R.A.R.D.E. (Engl), whose studies included techniques which allow for the recognition of fractured polymeric or steel fragments as having been generated by either low energy, high energy, or fatigue mechanisms. They also studied the particle size distribution and morphology of Mg powder used in pyrots, as well as paint pigments used for camouflage applications. They found the SEM an excellent tool in revealing imperfections in surface coatings such as ceramic glazes or phosphor coatings applied to heat treated steel parts. Additionally, faulty electronic circuits in shell fuzes were found to be caused by the growth of Sn whiskers. Examination of composite matrix interfaces such as Ni plated carbon fibers gave insights into fracture causation, based on both inherent weaknesses in the composite constituents, as well as on fissures and voids between the materials caused by low compaction (Ref 40).

More recently, the work of Beetle and Steward (Ref 49), using SEM, has shown it well-suited for studies of steel fracture surfaces produced by expl action. Several Si-Mn steels with selected, known microstructures were formed into cylinders and explosively fragmented using Comp B. The direct identification of such microscopic fracture modes as transgranular cleavage, radial fracture, intergranular separation or ductile dimpled rupture, was shown to be considerably more dependable by SEM than by OM.

Voreck of PicArsn applied SEM to the examination of detonator ingredients, which included a comparison of normal dextrinized Lead Azide (LA) which had been involved in so-called "spontaneous" expls vs "safe" LA. Although no significant differences were noted between the batches, the SEM revealed details of LA structure hitherto unobservable. In particular, 0.1 to 0.5 micron wide, onion-like, clearly defined growth rings were noted around individual seed crystals. In the course of the examination, holes some 3-6μ in diameter were burned into individual Au coated LA particles without causing detonation of adjacent material (Ref 44).

Mapes, at PicArsn, studied thin films of RDX using SEM (Refs 36 & 55). Much of the work was performed on uncoated specimens mounted on sapphire substrates, so as to provide some index as to the degree of crystallinity and morphology of the materials, per se. The SEM used in this work had a W field oriented emission source of four stages (with avalanche amplification) together with the conventional electron triode gun. The field emission source SEM operates under a much higher (clean) vacuum than conventional SEM's without contaminating the specimens. The field emission source enables the SEM to reveal lattice imperfections of 2.0Å at high resolution (Refs 58 & 59).

Other instruments which have been devised for microstructure examination include the X-ray microscope, with greater resolving power than the EM (Ref 41), and the electron microscope, capable of indicating subtle changes in composition over small specimen areas (Refs 57 & 62).

Written by H. L. HERMAN


Miedzianikat. A type of chlorate expls manufd in Ger and Poland prior to WWII. They typically contd K or Na chlorate 88–91 and liq hydrocarbons (with flash p not below 30°) 12–9% (Ref 1); K chlorate 90 and petroleum 10%; or K chlorate 87, petroleum distillate 10 and beechwood flour 3%. Their history, props and prepn are detailed in Ref 2 Refs: 1) Naoum, Explo (1927), 131 2) M. Winter, Kali 22, 161–4, 181–4, 201–5, 226–9 (1928) & CA 22, 4249 (1928) 3) Marshall 3, 112 (1932) 4) A. Perez Ara (1945), 207 5) Stettbacher (1948), 91


Military Biological and Biological Agents. See under Chemical, Biological and Radiological (CBR) Warfare in Vol 2, C171-R

Military Blasting Explosives and Military Demolition Explosives. See under Demolition Explosives, Vol 3, D56-R to D61-L

Military Blasting Gelatins. Explo used in Austria between 1878 and 1892 contg 96p of blasting gelatin (NG 90, Collodion Cotton 10%) and 4p of camphor. A similar expl was used in Russia during WWI for filling trench mortar rounds. It contd NG 90, Collodion Cotton 7 and cam-
Military Specification. A procurement specification promulgated by the military agencies and used for 'the procurement of military supplies and equipment. Typical contents include ingredients, formulae, tests, precautions, and acceptance marking information. The USA Dept of Defense Index of Specifications, Standards and related standardization documents is comprised of two separate parts: Part I — an alphabetic listing, Part II — a numeric listing, and Part II Appendix, contg a cumulative listing of canceled documents published triennially. The primary distribution agency is: Commanding Officer, Naval Publications and Forms Center, 5801 Tabor Ave, Philadelphia, Pa 19120, USA

Refs: 1) OrdTechTerm (1962), 192-R 2) G. Cohn, Ed, Expls&Pyrots 6 (3), March-1973

Military Standard (MIL Std). An authoritative USA Dept of Defense publication setting forth uniform procedures, definitions and standards for mandatory use thruout the Depts of the Army, the Navy, and the Air Force. See Military Specification for distribution source

Ref: OrdTechTerm (1962), 192-R

Millbank Explosives. Mining expls contg K chloride. Typical formulations contain K chloride 66.96, amorph P 3.75 and charcoal 29.29%; K chloride 64.30, K ferrocyanide 32.20 and charcoal 3.50%

Ref: Daniel (1902), 439

Miller Explosive. Consisted of two mixts, each of them relatively inert, but becoming an expl when mixed. They contd Na nitrate 35, K chloride 35 and starch 2ps, K dichromate 3, sulfur 13 and charcoal 12ps

Ref: Daniel (1902), 439

Mills Grenade. A pineapple-shaped fragmentation grenade, originating in Engl during WWI and adopted in the USA. The grenade used in WWII was a modified form, the Mark II. It has a cast iron body, serrated on the surface. It is loaded with TNT or other HE and has a time fuze with a delay element, a priming cap and a striker. When the grenade is to be thrown, the safety pin is removed and this causes the striker pin (held by a spring) to hit and ignite the primer compn and the delay element. After a lapse of 4–5 seconds, a detonator initiates the bursting charge, and the serrated grenade body splits into about 40 pieces on exploding

Refs: 1) Newman (1943), 62 2) Ohart (1946), 356

Mindeleff Explosive (Terrorite). Consisted of NG with various amts of methanol. It was used in Mexico for charging projectiles, but was found to be unsatisfactory

Ref: Daniel (1902), 440 & 765

Mines (Military). Originally mine warfare consisted of tunneling beneath impenetrable enemy positions and placing expls there to destroy them. This was known as sapping and dates back far in military history: Mine warfare did not become prominent, however, until WWI, when late in 1914 on the Ypres front, the Germans placed charges in tunnels dug under the British lines, which they fired at the opening of their attack. This had the effect the Germans expected. When their first assault wave reached the British position, the Germans found the British defenses so badly shocked by the explosions that they were able to pass thru without difficulty

Mine warfare as we know it today; however, began when the Germans produced or improvised land mines from artillery shells as a countermeasure against the newly introduced British armored tanks. These were detoned electrically when the tanks reached the mined area. At the same time the Allies also developed an antitank mine of artillery shells that deton under the weight of a tank. These German and Allied improvisations, though crude, were very effective

During WWII, as mine warfare was carried on widely by both sides, land mines were developed to a very high degree. They came to include a variety of antitank, antivehicle, dual purpose, and antipersonnel mines with a variety of fuzes.
Mine cases, at first made largely of steel, were later made from all sorts of nonmetallic materials. Today, many of the metallic and nonmetallic bodied mines are equipped with improved contact fuzes and influence fuzes that do not require direct contact with the target, and are thus difficult if not almost impossible to detect and disarm.

_Land mines_ are placed on land or just beneath the surface, to inflict damage on either personnel or equipment. They are of the trap type, being initiated by unsuspected action of the enemy. If they are for the purpose of destroying vehicles, trucks, and tanks, they are called _Antitank Mines_, and if they are directed against personnel they are called _Antipersonnel Mines_. _Beach Defense Mines_ are laid just under the water to defend beaches against landing craft. Since all mines, but particularly antipersonnel mines, can be hidden in a great variety of places and can be actuated in a variety of ways, some are called _Booby Traps_, because the "boob" or unsuspecting soldier may sit on something, pick something up, step on something, or trip over a wire, any one of which actions may actuate the mine.

_Antitank_ mines consist of an HE charge, usually 3 to 22 lbs, in a metallic or nonmetallic casing fitted with a primary detonator fuze, and usually secondary, antiremoval fuzes. Ordinarily, antitank mines require a press of 300 to 400 lbs to actuate them.

_Antipersonnel_ mines consist of a small amount of HE, generally less than 1 lb, in a metallic or nonmetallic container fitted with a detonator fuze arranged for actuation by press or release of press by pull on a trip wire, or by release of tension (cutting) of a taut trip wire. Two types are available, the blast type, which explodes in place, and the bounding type (_bouncing Betty_), which projects a fragmenting body into the air that, upon detonation, scatters fragments over a wide area.

_Naval mines_ contain a large amount of HE, and are deployed underwater for destroying passing enemy vessels. General types include _Ground, Moored, Magnetic_ and _Drifting_ mines. Ground mines possess considerable negative buoyancy and are intended to rest on the bottom. For this reason they are suitable for use in relatively shallow water only. Moored mines, in positively buoyant mine cases, are held at a predetermined depth below the surface by a cable or chain mooring attached to an anchor that rests on the bottom. Magnetic mines are intended to be detonated when the hull of a passing vessel causes a change in the magnetic field at the mine. Drifting mines are adjusted to float, unanchored, on or just below the surface of the water. A special type of drifting mine is the _oscillating mine_, which rises and falls gently as it continuously seeks its point of balance.

_Aerial mines_ are designed to be dropped from an aircraft, especially into water, hence, aerial minelaying, aerial mining, etc.

Although land mine warfare has been effectively used in recent conflicts, mines have not been used to their greatest potential advantage because of their limited versatility, being time consuming to emplace, and generally usable only in defensive situations on land controlled by friendly forces. The standard US _M15_ anti-tank mine weighs 30 lbs with 20 lbs of high explosive. It requires the manual insertion of the fuze just prior to use, and until the recent availability of a towed mine planter, could only be laboriously emplaced by hand. Another disadvantage in using standard mines like the _M15_ is that they frequently pose as much of a threat to the mobility of friendly as well as enemy forces. What was needed was a family of lightweight, effective, and rapidly emplaced mines which could be used in areas not under friendly control. In addition, to permit flexibility in their use, these mines should be capable of deactivation at a predetermined time after emplacement.

The _XM56_ mine system, aerially emplaced and scatterable, was developed in the 1960's as a response to these needs (Refs 14 & 15). The _XM56_ subsystem consists of an aircraft dispenser and the appropriate aircraft controls, as well as the mines themselves. It was designed to be carried aboard the _UH-1H_ helicopter which has a payload of 160 mines — 80 in each of two dispensers. The mine itself consists of an aluminum body in the shape of a half cylinder about 10 inches long and 4½ inches in diameter. It weighs about 6 lbs and carries a little over 3 lbs of explosive. The _XM56_ minefield will clear itself a predetermined time after emplacement by means of a self-destruct mechanism. The need for lengthy clearing procedures are thus eliminated.

Written by **S.M. Kaye**

Refs: 1) Newman (1943), 203, 218, 226 & 267
  2) Ohart (1946), 9, 135, 363–70
  3) Anon, "Land Mines", _TM 9-1940_ (May 1956)
  4) OrdTechTerm
Anon, "Foreign Mine Warfare Equipment", TM 5-280 (April 1963)
6) Anon, "Mines, Land: Identification; Care; Handling and Use", TM 9-1345-200 (June 1964)
7) Collier's Encycl, "Naval Mines"; 17, 231-235 (1965)
8) Anon, "Mine, Antipersonnel, PWP, Pop Up, SM54", TM 3-1345-205-10 (Sept 1968)
9) Anon, "Mine, Special Purpose, Claymore", TM 9-1385-212 (Dec 1968)
12) Anon, "Mines, Antitank (HE, Heavy), M15", TM 9-1375-200/2 (June 1971)
14) Anon, "New Dimension Added to US Mine Warfare", AMC News 2, No 9 (July 1974)

Mine Clearing Equipment. Devices used to actuate land mines without damage to personnel or equipment. Expl devices are typified by a group of linear shaped prefabricated structural sections, filled with composition expls, with a nose section and a towing and pushing attachment, designed for assembly into a device to be propelled by any standard tank. It is designed to breach a path thru a mine field upon the deton by fire from the pushing tank's machine guns, of the linear shaped charges (Ref 1). Earlier designs were termed snake, demolition (Ref 3)

Mechanical devices include the Brit Scorpion, the US Mine Exploder T1E3 (Ref 1) and a Russ tank-mounted mine clearing roller (Ref 3). The Scorpion consisted of a horizontal drum, rotating (by means of a drive connected to the tank engine) between two long beams attached to the front of a medium tank. Several long, thin bars were attached to the drum, with length of chain attached to the end of each bar. As the drum rotated, the chains whipped the ground, initiating any concealed tank mines. The US T1E3 Exploder consisted of a series of armor-plate steel discs, 8 ft in diameter, mounted loosely on a horizontal shaft, which was attached to two beams extending in front of a tank. These discs were quite heavy (30 tons), and rolled along the ground before the tank, exploding all mines over which they passed. Recent Russ models of rollers and flails clear two wide tracks, each about 2 meters wide, for the passage of tanks and other vehicles (Ref 3)

Refs: 1) G.M. Barnes, "Weapons of World War II", D. Van Nostrand Co, NYC (1947), 96-97
2) Anon, "Land Mines", TM 9-1940 (May 1956), 07-109
3) OrdTechTerm (1962), 193-R
4) Anon, "Foreign Mine Warfare Equipment", TM 5-280 (April 1963), 962-3

Mine Detector. Devices, usually electrical or magnetic, used to locate metallic mines. Man portable units consist of a search coil housed in a detector head assembly, a search handle, control box, oscillator amplifier, batteries, headphones and tuner. They operate on either induction or heat frequency principles. In the latter, the tone in the earphones changes in pitch rather than in volume; a buzzing sound occurs only when the search coil is held over a metallic object (Ref 2). A jeep-mounted mine detector which automatically stops the vehicle when it locates a land mine is described in Ref 1

2) Anon, "Foreign Mine Warfare Equipment", TM 5-280 (April 1963), 921-950

Mine, Poudres de. BkPdrs manufd in Fr beginning in 1900 for use in mines. Their shape was either angular or round, and they were divided into three classes: strong (forte), ordinary (ordinaire) and slow (lente). K nitrate content ranged from 72.62% for "forte" to 40% for "lente". A special "lente" pdr contd K nitrate 65, sulfur 15, charcoal 10 and sawdust 10%

Ref: Daniel (1902), 440

Minèlites. Expls developed in Fr and found to be satisfactory by the Commission des Substances Explosives. Their compn and props are given below
Minérite. A Belg safety expl which has the same compn as the Ger expl, Kohlencarbonit (qv)
Ref: Marshall 1, 376 (1917)

Miner's Friend. A lignin Dynamite, formerly manufd in the USA by the Hecla Powder Co. It contd varying amts of NG together with lignin and Na nitrate
Refs: 1) Daniel (1902), 440 2) Thorpe 2, 439 (1918) 3) Van Gelder & Schlatter (1927), 659

Miner's Safety Explosive (Explosif de Sûreté). The name under which "ammonites" were originally known
Ref: Daniel (1902), 441

Miner's Safety Fuse (Méches de Sûreté). See Bickford Safety Fuse

Miner's Safety Fuse Matches (Allumeurs de Sûreté). See under Igniters for Fuse

Miner's Squib (Pétard de Mineurs). One of the primitive devices which was invented by Daddow in Engl in 1874 for igniting blasting expls. It consists of a tapered paper tube, about 7 inches long, filled with fine gunpowd. One end of the tube is filled with chemicals, such as milled gunpowd mixed with either sulfur or sulfur and charcoal, so as to form a sort of slow match. A little gunpowd is added at the end in order to facilitate ign of the slow match. When used, the squib is inserted with the slow match outward in a hole made in a charge of BkPdr blasting expl. When the match is lit, the fire burns slowly, allowing the miner time to reach a place of safety. As soon as the fire reaches the BkPdr core of the squib, it burns fiercely and then suddenly explodes, igniting the blasting expl. Instead of the paper tube, quills filled with fine BkPdr joined to a slow match, can be used

Hunter (Ref 1, p 379) proposed, in 1882, a squib which resembled that of Daddow, except that the tube contg the BkPdr was varnished on the outside
According to Marshall (Ref 2), there were also devices called German Spills, which resembled Daddow's squib, but no description of them is given.

It should be noted that all of these devices are dangerous and not very reliable. Their use, being against the regulations of most countries, can only be justified when no other devices are available.

Refs: 1) Daniel (1902), 379, 441 & 611
2) Marshall 2, 539 (1917) 3) Barnett (1919), 173–74

Minex. One of the variations of DBX (Depth Bomb Explosive). It consists of TNT 40, RDX 5–15, AN 35–25 & Al pdr 20%. It is a gray solid with a cast d of 1.68g/cc and a mp of 80–90°, which permits cast loading. Its props are similar to that of DBX (Ref 2). Refs: 1) All&EnExpls (1946), 130 2) Encycl 3 (1966), D19-L

Miniature-Cartridge Test. For quantitatively evaluating the relative initiating efficiency of detonators. The test is based on the principle that the ability of a detonator to initiate an insensitive expl is the best criterion of its initiating efficiency. The insensitive expl used for this purpose is a mix of 70–80% TNT and 30–20% Fe2O3. The degree of deton of the mix is detd by means of a modification of the Sand Test (qv). A 5g charge of the mix is packed to a const diam around the detonator in a paper cartridge, and the assembly is deton in the center of 1000g of standard Ottawa sand in a steel bomb 3 inches in diam. The crushed sand which passes thru a No 30 sieve is a measure of the energy of the deton, less a correction for the detonator in Fe2O3.


Miniature Conductive Mix Detonator. Since conductive mix detonators would have no bridge wire, which is a delicate and expensive step in the manuf of bridge wire detonators, it has been proposed that conductive mix detonators would provide an attractive alternative to bridge wire units from standpoints of economics and reliability. A typical DuPont conductive mix detonator is 0.14 inch in diam by 0.292 inch in length, uses pin and cup for electric contacts, and contains a DuPont conductive mix, LA and an output charge of HMX. It is designed to fire from a 2.2 microfarad capacitor charged to 15V. Output is sufficient to initiate pressed Tetryl over an 0.045 inch air gap thru an 0.008 inch thick barrier of mild steel.

Refs: Explosives Products Division, E.I. DuPont de Nemours & Co, Wilmington, Delaware & G. Cohn, Ed, Explos&Pyrots 6 (6), (1973)


Minite. A Belg permissible expl of the “Carbonit” type, NG 25, K nitrate 35, flour 39.5, Na carbonate 0.5%. Charge limit is 750g, equiv to 405g of Brit Standard Gelignite. According to Gody (Ref 2) it is called Minite d’Arendonck. According to Daniel (Ref 1) one of the minites was a Dynamite contg NH4 sulfate.

Refs: 1) Daniel (1902), 441 2) Gody, Explosifs (1907), 714 3) Marshall 1, 376 (1917) 4) Barnett (1919), 140

Minol (Ammonal, Alumatol, Burrowite). Minols are explosive mixtures containing aluminum, ammonium nitrate (AN) or a mix of AN and potassium nitrate (KN), and TNT. The Ammonals (see Vol 1, A287-L to A293-R), forerunners of the Minols, were developed prior to and during WWI because of a scarcity of TNT. At that time they were not highly regarded because of a nonrealization of the effectiveness of alumized expls, coupled with the high cost and nonavailability of Al. Ammonals were used as shell fillers for their fragmentation effect (Ref 8), but were later found to be inferior to Minol II (see below) with respect to blast and shock effects, and less brisant than Composition B (see Vol 3, C477-R to C484-L).

During WWII, the plentiful supply of TNT...
in the USA rendered the use of Ammonials unnecessary, and the development of expls having
great blast effects rather than brisance led to
the use of Tritonal by the US and of Minols by
the United Kingdom (UK). The UK used the
following three Minol formulations during WWII
(Refs 8 & 21):

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Minol I</th>
<th>Minol II</th>
<th>Minol III</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>48</td>
<td>40</td>
<td>42</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>42</td>
<td>40</td>
<td>38</td>
</tr>
<tr>
<td>Aluminum</td>
<td>10</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

These Minols were prepd by adding appropriate quantities of dry AN and Al powder to
molten TNT at 90° under agitation. Minol II
could be prepd by adding 25 parts of Al to 100
parts of 50/50 Amatol, or the calculated
amounts of ingredients to other Amatols pre-
viously prepd.

Minols are gray in color, have densities ranging
between 1.62 and 1.74g/cc, and are cast loaded.
They resemble Torpex in explosive properties,
but are less brisant. They exhibit dimensional
instability when exposed to thermal cycling
during long term storage.

In 1945, all bombs, depth charges and mines
were loaded with Minols in the UK (Ref 21).
Undesirable gassing and spewing, as well as ex-
pansion of the Minols were encountered on
mixing or after loading into ordnance. Limited
expl work indicated that the Al-water reaction
could contribute significantly to spewing and
would be markedly enhanced by impurities in
the Al. These undesirable phenomena were ob-
cerved coincident with the adoption of Minol II,
having double the amount of Al powder and with
the introduction of a lower grade of Al (Ref 31).
The Al reactivity was reduced thru the use of a
"biscuit" technique (addition of chunks of solid
expl to the melt to reduce the temp), and better
control of the pouring temps (Ref 21). In
manuf of Minol II, the Al particle size range
first used in the UK was "120 mesh to dust".
This was later changed to a coarser "36 mesh to
dust" fraction in order to obtain increased pro-
duction, remove dust hazards and decrease the
chemical reactivity of the Al (Ref 21).

During the Vietnam conflict, the USA utilized
Minol II in general purpose (GP) bombs, and en-
countered a milder form of spewing which was
termed oozing. The cause of this occurrence was
ever determined, although the hygroscopicity of
AN and volume changes associated with its poly-
morphic transitions were considered contributing
factors (Refs 17, 23, 26, 29 & 47; also see under
Ammonium Nitrate in Vol 1, A311).

Recent studies (Ref 46a) indicated that water
did indeed enhance the gassing of Minol at temps
above 75°, but that this gassing represented less
than 0.1% of decomp in the mixt, and would be
a small volume of gas relative to the mass of expl
in a munition. At the present time, therefore,
the cause(s) of spewing or oozing are still not
known.

The excessive growth of Minol II in the field
during storage was also a problem in Vietnam. It
has been speculated that such growth could have
been caused by gas producing reactions between
AN and Al, AN and TNT or Al and water (Ref 45),
but it is considered by many that the ob-
served growth was the result of volume changes
resulting from the polymorphic phase transition
between form III (gamma) and form IV (beta)
AN (Refs 1, 3, 4, 5, 9, 10, 11, 12, 14, 16, 17, 18
& 19). It was also found that Minol II grows
more when low set-point, continuous process
TNT is used, and when CP grade AN is employed
in the mix (Ref 40). The greatest chemical and
mechanical stability over the ambient temp to
100° range was obtained when dry, "Product
A", large-grained AN was employed (Ref 36).

At elevated temps (<90°), Minol II reacts with
inert sealing compound and asphalt-based coa-
tings used in bomb cavities. Asphalts contg free
S, unsaturated compds, V and Cu are particular-
ly reactive with Minol II (Ref 35). A new coa-
ting, a polypropylene base hot melt was found
suitable as a replacement cavity liner for the
750lb M117A1 GP bomb (Ref 41). This new
liner material is basically a mixt of amorphous
polypropylene wax and rosin. It is completely
compatible with Minol II, and can be used in
place of the hot melt asphaltic compd presently
used. Another liner material, primer paint, has
been reported to reduce growth and exudation
when used as an interior coating in bomb casings
(Ref 40).

The particle density and bulk density of AN part-
culates (prills, granules, pellets) are reflected in
the density of the cast Minol II prep. The
highest Minol II density is attained thru use of
grained AN which has the highest particle and bulk density (Ref 48)  

AN particle shape, size distribution and density have a significant effect on the mixing and loading characteristics of molten Minol II. The product made with grained AN was best with respect to ease of mixing, smooth consistency, uniform viscosity, pourability and cast density (Ref 48)  

Unlike grained AN, which is virtually uncoated, prills and other forms of AN, as marketed commercially, are coated with substantial and varying amounts of clay, talc, diatomaceous earth, or a mixt of one of these with various organic additives, used to inhibit or retard “caking”. Not all of these coating agents are compatible with the Minol ingredients, and each coating material must be checked prior to use to determine that it is compatible (Ref 48)  

In addition, manufacturers have attempted to phase-stabilize AN by adding small amounts of boric acid, diammonium phosphate and ammonium sulfate prior to crysint. It was hoped that this stabilization of AN against change from one solid phase to another, with accompanying change in volume, might minimize the Minol II growth problem (Ref 48). Recent studies have shown that both coated and uncoated, phase-stabilized, high density AN can be used in Minol II. However, Minol II charges made with grained AN have the highest detonation velocity compared to charges made with other forms of AN (Ref 48)  

It is well known that AN slowly evolves ammonia on storage, particularly in the presence of moisture. In the presence of Al, this evolution is markedly greater. The evolution of ammonia is particularly undesirable in mixts such as Minol II, inasmuch as TNT has been reported to form a readily ignitable compound when treated with concd aq ammonia (Ref 28). Unfortunately, there has been no detailed study of the TNT–NH₃ reaction, and there is no evidence that this reaction can occur in solid Minol  

Originally, the Al used in Minol II was in the form of a fine powder. It was shown later that such a high degree of sub-division was unnecessary, and that good performance could also be achieved with Al filings, shavings and flakes. The latter form is particularly advantageous in that the smaller total surface area of Al present in the mixt minimizes its reactivity in Minol and enhances the chemical stability of the compn (Ref 28)  

Minol II expands more and exudes less than TNT or Tritonal under similar temp cycling conditions (Ref 40). The exudation of inert sealer in connection with bomb fills has been a problem since 1945, when an inert sealer pad was adopted as a safeguard against impact initiation. The exudation products appeared to be a mixt of wax sealer and black asphalt, and contained no expl. The use an inert, compressible material in place of the inert wax in GP bomb tail sections, along with better sealing, has been successful in overcoming such exudation (Ref 32)  

It has been reported that dry Minol II is stable and unreactive when cycled between ambient temp and 100°C, and if prep'd with dry AN, does not show a phase transition under 50°C. However, when AN is used which is not thoroughly dry, Minol II will exhibit a reversible phase transition beginning at 32°C, producing volume changes of about 3.8%. These volume changes could cause microcrystalline cracks and pores which could reduce detonation velocity and mechanical strength (Ref 36)  

In addition to the above chemical reactivity and dimensional stability problems, Minol II exhibits borderline initiatibility at −65°F with small boosters, but initiates reliably at low temps with standard larger boosters (Ref 43)  

In an effort to overcome the dimensional stability problem, recent work has been directed toward substituting a solid soln of K nitrate (KN) in AN (AN–KN or KN–AN form III) for the AN in Minol II. Charges containing 40% TNT, 40% AN–KN and 20% Al (designated Minol IV) did show better dimensional stability during temp cycling than either TNT or 67/33 TNT/Al (Ref 45). The 90/10 AN–KN samples were readily prepared in the laboratory and in prilling towers using existing AN technology.  

The use of 90/10 AN–KN in place of AN in Minol greatly delays the onset of charge growth and minimizes this growth (Ref 45). However, it has been found that growth still does occur, and charges subjected to very many thermal cycles will ultimately begin to crack, as does Minol containing AN. Raising the KN concn to 20% in AN–KN provides a Minol with no detectable growth or cracking after months of cycling, but such a Minol has not been qualified for service use  

Table I details the physical, chemical and explosive properties of Minols II and IV
### Table 1
Properties of Minol II and Minol IV

<table>
<thead>
<tr>
<th>Property</th>
<th>Minol II</th>
<th>Minol IV</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading density (cast), g/cc</td>
<td>1.62–1.68</td>
<td>1.793</td>
<td>37, 49</td>
</tr>
<tr>
<td>Air Blast (relative to TNT)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak pressure</td>
<td>115</td>
<td>—</td>
<td>19</td>
</tr>
<tr>
<td>Impulse</td>
<td>116</td>
<td>—</td>
<td>19</td>
</tr>
<tr>
<td>Energy</td>
<td>133</td>
<td>—</td>
<td>19</td>
</tr>
<tr>
<td>Brisance by sand test, grams</td>
<td>40.5</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>(86% of TNT)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Booster Sensitivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressed density, g/cc</td>
<td>1.74</td>
<td>—</td>
<td>20</td>
</tr>
<tr>
<td>Wt of Tetryl pellet, grams</td>
<td>100</td>
<td>—</td>
<td>20</td>
</tr>
<tr>
<td>Max inches for 50% detonation</td>
<td>1.46</td>
<td>—</td>
<td>20</td>
</tr>
<tr>
<td>Brisance by Plate Dent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unconfined</td>
<td>66% of TNT</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>Compressive Strength, lb/sq in</td>
<td>1910–2070</td>
<td>—</td>
<td>15</td>
</tr>
<tr>
<td>at density, g/cc</td>
<td>1.68</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Cook-off (large scale)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Less sensitive than H-6 or Comp B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detonation Velocity, m/sec</td>
<td>5900</td>
<td>5900–6000</td>
<td>5, 49</td>
</tr>
<tr>
<td>Electrostatic Sensitivity, 20/20 no fires at 0.25 joules</td>
<td>Passed</td>
<td>Passed</td>
<td>49</td>
</tr>
<tr>
<td>Explosion Temperature, 5 second</td>
<td>435°</td>
<td>—</td>
<td>35</td>
</tr>
<tr>
<td>Flammability Index</td>
<td>100</td>
<td>—</td>
<td>35</td>
</tr>
<tr>
<td>Fragmentation Velocity</td>
<td>100% of TNT</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>Friction Sensitivity, 20/20 no fires at 250 lb force</td>
<td>Passed</td>
<td>Passed</td>
<td>49</td>
</tr>
<tr>
<td>Growth and Exudation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>on thermal cycling between −54° and +60° for 30 cycles</td>
<td>Charge 9.92%, completely disintegrates</td>
<td>no measurable exudation</td>
<td>49</td>
</tr>
<tr>
<td>Heat of Combustion, cal/g</td>
<td>3160</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>Heat of Explosion, cal/g</td>
<td>1620</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>Impact Sensitivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA App with 2kg wt, inches</td>
<td>13</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>sample wt 17 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BurMines App, cm</td>
<td>35</td>
<td>—</td>
<td>37</td>
</tr>
<tr>
<td>sample wt 20 mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qualification tests, cm</td>
<td>73</td>
<td>55</td>
<td>49</td>
</tr>
<tr>
<td>Large Scale Gap Sensitivity, cards</td>
<td>140</td>
<td>107</td>
<td>49</td>
</tr>
<tr>
<td>Power, by Ballistic Mortar</td>
<td>143% of TNT</td>
<td>—</td>
<td>13</td>
</tr>
<tr>
<td>by Trauzl Test</td>
<td>165% of TNT</td>
<td>—</td>
<td>15</td>
</tr>
</tbody>
</table>

(continued)
Table 1 — Properties of Minol II and Minol IV (continuation)

<table>
<thead>
<tr>
<th>Property</th>
<th>Minol II</th>
<th>Minol IV</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rifle Bullet Sensitivity, affected, percent</td>
<td>48</td>
<td>—</td>
<td>8</td>
</tr>
<tr>
<td>Self Heating</td>
<td>—</td>
<td>No temp exotherms from ambient to 170°</td>
<td>49</td>
</tr>
</tbody>
</table>

Specific Heat
- density, g/cc: 1.74
- at -5°C, cal/g/°C: 0.30

Thermal Conductivity
- density, g/cc: 1.74
- cal/sec/cm/°C: 16.5 x 10^-4

Vacuum Stability Test
- cc gas in 40 hrs at 120° from 5.0g sample: 2.1
- cc gas/g sample in 48 hrs at 100°: 0.00, 0.05

Young’s Modulus
- density, g/cc: 1.66
- E’, dynes/sq cm: 5.03 x 10^10
- E, psi: 0.73 x 10^6

Uses. Minols have historically been used in four types of ordnance, a) underwater (mines, torpedoes and depth charges) where the confinement of water offsets some of the loss of detonation velocity, b) “blockbuster” bombs in which a sustained and powerful impulse is more destructive than a high peak press, c) concrete fragmentation bombs where the high impulse will impart a satisfactory fragment velocity but will not pulverize the concrete they contact on impact, and d) in general purpose (GP) bombs.

The quantitative analysis procedure involves benz extr of TNT, water extr of AN, and taking of the AI content as insol residue. Moisture content is detd by the Karl Fischer method described in ASTM Method E203-62, except that 8 to 10g samples are added to methanol. Specific gravity is detd by water displacement, and workmanship by visual examination.

Written by J. HENDRICKSON


Addnl Refs Not Used in Above Article:

Minolite Antigrisouete. A Belg coal mine expl considered safe for use at charge wts up to 650g. It contains AN 72, Na nitrate 23, TNT 3 and TN-Naphthalene 2% Refs: 1) Anon, SS 3, 337 (1908) 2) Marshall 1, 390 (1917) 3) A. Pérez Ara (1945), 243

Minolites. Exps manuf by Cornet & Verviers in Belg since 1897. One of the later compnts cont AN 87, Na nitrate 3, DNNaphthalene 3, TNNaphthalene 5, sawdust and resin 2%, and has a calcd temp of expl of 1916° Ref: Daniel (1902), 441

Minuteman. US intercontinental ballistic missile series (see Ballistic Missile in Vol 2, B6). They are three-stage missiles with solid propilt motors designed as simplified and low cost weapons for launching from silo sites. The first production model was assembled in Apr 1962, and since then 1000 Minuteman missiles, in three versions, have become operational. A new version (Minuteman 3) with multiple warheads has also been developed. LGM-30A (Minuteman 1) is 53ft, 9 inches long, weighs about 60000 lbs and delivers a megaton warhead over 6000 miles at a speed of about Mach 22, utilizing an inertial guidance system. The warhead is armed only after the missile is airborne. LGM-30B is a little longer, heavier and more precise than the LGM-30A. These were subsequently phased out by the LGM-30F (Minuteman 2), which is 50ft, 10 inches long, weighs 70000 lbs and has a 7900 mile range. Instead of the swivelling quadruple
nozzles of the two earlier types, it has a liq-

injection single nozzle system. The Minuteman 2
has a two-megaton warhead, and became opera-
tional in 1966. A Minuteman 3 with MIRV
(qv) multiple warheads is currently being pro-
duced, and is reported to carry three 0.2 mega-
ton warheads

Refs: 1) E. Luttwak, “A Dictionary of Modern
War”, Harper & Row, NY (1971), 130
2) Encyl Britannica 19, 403–24 (1973)

MIRV. Acronym for Multiple Independently-
Targetted Re-Entry Vehicle. A single missile
can dispense several warheads, each of which
is separately guided to its target. MIRV warheads
were developed with the intent of improving
ICBM cost-effectiveness. USA MIRV’s include
the Minuteman 3 and the Poseidon

Ref: E. Luttwak, “A Dictionary of Modern
War”, Harper & Row, NY (1971), 131–32

Mischdynamit. A typical nongelatinous Dyn
contg NG 40, Na nitrate 45, wood meal 12,
carbonate & moisture 3%

Ref: Beyling & Drekopf (1936), 89

Misch Metal. An alloy of rare earths of the fol-
lowing approx compn: Ce 49, La 25.6, Nd
16.0, Pr 4.6, Sm 2.0, Tb 1.0, Y 1.0 & Fe 0.8%.
The powd alloy was patented as an ingredient
of delay compns used in delay elements for
electric blasting caps. Other ingredients included
Mg, Al, Ni & Zr homogeneously mixed with a
fuel such as Si and Pb2O4 as oxidant (Ref 1).
Misch metal, ground under xylene in small
ball mills and incorporated into bridgewire
sensitive ignition mixts as well as in some delay
formulas, was still in use in Ger in WWII (Ref 2)

Refs: 1) H.M. Kerr & C.R. Hall, USP 2560452
(1951) & CA 46, 1259 (1952) 2) Ellemer
(1968), 34–35

Missile (Guided, Non-Ballistic). An unmanned
and disposable vehicle which is guided to, rather
than aimed at its target. They differ in this
principle from Ballistic Missiles (see Vol 2 of
Encycl, B6), which are guided during powered
flight in the upward part of their trajectory,
and become free falling bodies subject to the
laws of ballistics, in the latter stages of their
flight toward targets

Non-ballistic missiles are usually classified as:
Air-to-Air (AAM), used as aircraft-to-aircraft
weapons to supplement or replace guns; Air-to-
Surface (ASM), a larger category, which includes
stand-off missiles, antiradiation missiles such as
Shrike, as well as ordinary ASM’s; Surface-to-
Air (SAM), are anti-aircraft missiles ranging
from the man-portable Redeye to the long-
rang Bomar, and include anti-missile missiles
such as Sprint, Spartan and Galosh; Surface-
to-Air, includes non-ballistic nuclear bombard-
ment missiles such as Mace B, as well as the
separately listed ballistic family; also includes
small non-nuclear anti-tank missiles and naval
missiles such as the Rus Styy, and Anti-Subma-
rine, typified by Astro, Subroc and Ikara (Refs
4, 5, 8 & 9)

Infra-red homing is used in many air-to-air
and some anti-aircraft types such as Sidewinder,
Red Top and Redeye. Since it relies on optical
radiation, this form of guidance is short range
and dependent on reasonably clear skies

Semi-active radar homing units consist of a
narrow-beam tracking radar receiver which
“locks on” the target, and a computer which
generates flight-correction signals for the servo-
controls. In semi-active systems, the target is
“illuminated” by a radar transmitter on board
the launching ship or aircraft, or, in the case of
surface-to-air missiles such as the Hawk, on the
ground

Active radar homing, where the missile has a
complete transmitter-receiver set, is a method of
guidance suitable only for rather large missiles.
Unlike infra-red homing, it is usable in all
weathers and at night. This type of guidance
can be used only against targets which have a
clear radar image when opposed to their back-
grounds, such as aircraft or ships (Refs 4, 8 & 9)

Radio-command is generally used in air-to-
ground systems, where the target is invisible to
radar because it blends into the ground image.
In the simplest form, the operator observes
visually both target and missile, and directs the
latter by joy-stick controls transmitted to the
missile by radio or along a wire link (Fr
AS.20/AS.30 & US Bulpup). Many ground-to-
ground anti-tank missiles use a variation of this system, where the signals are transmitted from the pilot to the missile by a thin wire uncoiled from the missile in flight. More sophisticated radio-command methods employ remote observation by TV, as used in the US Walleye, or infra-red assisted tracking of the missile, as in the US Tow. Radio command systems which do not rely on visual observation are employed in longer-range anti-aircraft and anti-shipping missiles, and in ballistic missile defense. In these, the missile is flown by remote control on the basis of data provided by radar tracking both target and missile. Radar is also employed in two other guidance methods: beam-riding, where the missile "rides" or tracks a pencil point beam directed at the target (Brit Seaslug), and comparative radar-mapping (US Mace & Mato- dor). In the latter, a high definition air-to-ground radar maps the ground over which the missile is flying, and compares the ground image with a recorded image stored in the memory of its computer. The computer compares the two images and, if the ground image picked up deviates from that stored in its memory, it actuates servo-controls to make suitable adjustments in its flight (Refs 7, 8 & 9).

Early missiles, from the Ger V-2 to the first generation of nuclear delivery vehicles (such as the US Atlas) were generally powered by liq-fueled rocket motors. The liquids used were highly unstable and could not be stored inside the missile, requiring lengthy fueling before launch. Storable-liq fuels were introduced in the next generation of missiles (US Titan II & Rus SS-9), and are still used on many missiles including most Rus ICBM's. Most missiles today are propelled by solid fuel motors, which are generally more reliable and economical than liq-fueled ones. Since most missiles require a powerful initial thrust for lift-off and a substantially weaker sustaining thrust, different "stages" are generally used, a powerful "booster" and a longer acting but less powerful "sustainer". More recently, dual-thrust rocket motors have been evolved; these are single-unit motors which can modify the thrust to fit different phases of flight (Ref 9).

Missile payload varies from nuclear, through HE fitted with proximity fuzes, to chemical warheads. Electronic countermeasures equip-

ment is an increasingly important part of missile payloads, mainly intended to deceive or confuse enemy radar surveillance and tracking (Ref 8).

Also see Vol 6, G178-L under Guided Missiles

Written by S. M. KAYE


Mist and Spray Explosions. See FAE & FAX (Fuel-Air-Explosives) in Vol 6, F3-L-F4-R

Mittasch Stability Test for Nitrocellulose. A test based on the measurement of press developed on decomp of NC. The app may be considered a very complicated modification of devices originated by Abel (Ref 4, p 241) and Hess (Refs 1 & 4). Abel heated NC samples in vac and detd the press increase. Hess believed that on heating NC in a closed vessel contg air, connected to a Hg manometer, it would be possible to achieve conditions more closely resembling those in storage in closed magazines. Neither of these methods found any practical application.

Mittasch, recognizing the fact that decomp of NC in Hess's app was abnormally high because the gases under press exercised an autocatalytic action, constructed an app in which NC, heated to 70° under atm press, was connected to a manometer. Thus, any vol changes because of gas formation were automatically registered. As Mittasch's app was very complicated and costly, it did not find practical application except in Engl, where it was used in modified form for
testing "cordites". This modification is described in detail by Kast & Metz (Ref 4, p 313)
Refs: 1) J. Hess, MiltArtuGeniew 10, 360 (1879) 2) J. Mittasch, ZAnChem 16, 929 (1903) 3) Reilly (1938), 87 4) Kast-Metz (1944), 241 & 313

Mixed Acids. See under Nitration in this Vol

MJ Powder. An experimental double-base proplnt developed during WWII contg NC 48.0, NG 31.0, K nitrate 17.5, carbon blk 2.5 & et centralite 1.0%
Ref: F.H. Westheimer, OSRD 4758 (1945), 10

M.N. An old US proplnt, invented by Maxim-Nordenfält, contg NC gelatinized by et acet. It was also manufd in Italy as "N57"
Ref: Daniel (1902), 442

MNO (N,N'-Dinitrodimethylxamide), C₄H₆N₄O₆; mw 206.14, N 27.20%, OB to CO₂ = 38.8%, mp 123°, d 1.52 g/cc. Can be prepbd by treating dimethoxyamide with HNO₃ or mixed acid (Ref 1). Pb block expansion is 110% PA or 110–115% TNT; BalMort is 116% TNT; deton vel is 5050m/sec at d 1.0 g/cc, 7050m/sec at d 1.5g/cc (Refs 3 & 9). Impact sensitivity is approx 0.9 TNT; Qₜₐ₈ 508.4, Qₚₐ₈ 511.9cal/mole (Refs 4, 5 & 6). Storage at 100° for 30 days produces no red fumes (Ref 9) and 6 month storage at 65° causes no decrease in stability (Ref 8). MNO is stable to hot concd HCl; with alkali furnishes salts of methylnitramine; with w develops acidity. At 25° it gains 0.03% at 90%, and 0.2% at 100% rel humidity (Ref 7)

MNO has been evaluated as being between Tetryl and TNT in performance, but of considerably lower stability because of a hydrolytic action with w (Ref 5). It is reported to form a eutectic with PETN, having the compn MNO 30, PETN 70%, which is liq at 100° and which, cast, passes a rifle-bullet test (Ref 3). A detailed study of the expi properties of MNO is given by MacDougall (Ref 5). MNO and analogous alkylidinitrooxamides are claimed to be less sensitive and as powerful as PA (Ref 2)

Also see under Dimethoxyamide and Derivatives in Vol 5 (1972), D1359-R to D1361-R

Moddite (Modite). A variety of "Cordite" manufd in the form of strips by Eley Brothers of Engi for use as sporting rifle proplnt. It contd NC (about 35% sol in eth-alc) 56.8, NG 38.7, mineral jelly 4.3 & vol matter 0.2%
Refs: 1) Marshall 1, 308 (1917) 2) Barnett (1919), 79

Model Designations. In order to identify a particular ammunition design in the USA, a model designation is assigned at the time the model is classified as an adopted type. This model designation becomes an essential part of the standard nomenclature and is included in the marking on the item

Prior to WWI, the number of the year in which the design was adopted preceded by an "M" was used as the model designation; for example, M1906. From WWI until July 1, 1925, it was the practice to assign mark numbers. The word "Mark", abbreviated "Mk", was followed by a roman numeral; for example, Shell, HE, Mk III. The first modification of a model was indicated by the addition of M1 to the mark number, the second by MII, etc. The present system of model designation consists of the letter "M" followed by an Arabic numeral, for example, M1. Modifications are indicated by adding the letter A and the appropriate Arabic numeral. Thus, M1A1 indicates the first modification of an item for which the original model designation was M1. Wherever a B suffix appears in a model designation, it indicates an item of alternative design, material or manuf. AT or XM model designation signifies that the item is
under development. An E with an Arabic numeral signifies a modification thereof. Ammunition developed by other services use other systems, eg, Mk-Mod system for US Navy materiel


Modernization Engineering Project for US Army Ammunition Plants. The US Army Munitions Command (MUCOM), in 1970, had 27 ammo production facilities located throughout the US to support the Government's military ammo needs for standard-type ammo for the military services. These plants were Government-Owned Contractor-Operated (GOCO), and were engaged in the manuf of prop plants and expts, metal parts and small arms ammo, and the load, construction and pack (LAP) of ammo. The purpose of the ammo plants complex was to provide reliable ammo production capability which would match established mobilization objectives in a timely and economical manner. The majority of the GOCO plants were built in the early 1940's, were operated in WWII, were activated during the Korean conflict, and were used to support the Government's requirements in the hostilities in Southeast Asia. These plants, in many instances, were built on an emergency basis, and had been operated far beyond their designed capabilities and life expectancy. Little had been done to modernize them. Early in 1968, MUCOM detd that an accelerated and revised modernization program was required for approx 22 of the production plants to overcome evident shortcomings and deficiencies. MUCOM modernization committees were formed to cover Propellants and Explosives (P&E), LAP, Metal Parts (MPTS), and Small Arms (SA) GOCO plants. These committees provided guidance regarding the technology priorities and the overall time phases of modernization plans for each MUCOM GOCO facility, and identified those areas where additional technological advances were required.

On June 30, 1969, MUCOM awarded a contract to Kaiser Engineers, in association with A.T. Kearny & Co, Inc, management consult-ants and industrial engineers, and Stetter Associates, Inc, industrial equipment consultants, to perform a comprehensive modernization engineering study of the GOCO ammo production plants during a one-year period. The project was developed under two separate but coordinated tasks: (1) Establishment of modernization master plan, and (2) Project modernization control. The objectives of the first task was to establish a modernization program for the GOCO ammo plants which would enable production of the then current and mobilization requirements for ammo in the most efficient, economic and expeditious manner utilizing the latest proven state-of-the-art in manuf processes. Under the second task, the objectives were to develop an integrated modernization master plan for the GOCO plant complex, establish a Master Facilities Data Bank with procedures for maintenance, data insertion and retrieval, and determine the feasibility of establishing an economic model and a priority system to facilitate management decisions on modernization.

The contract effort required a modernization plan report by ammo category and by GOCO plant. The ammo category report was to contain modernization planning considerations (including an assessment of current and advanced technol-ogy), and the recommended modernization master plan for all the GOCO plant production facilities with capabilities to produce items in the particular ammo category. Separate ammo category report volumes were to provide for LAP, P&E, MPTS & SA. Plant reports would treat the modernization planning applicable to a particular plant, reflecting the conclusions reached in ammo category-wide planning. Individual plant reports were to cover each GOCO plant designated by MUCOM for consideration.

A summary volume (Ref 1) provides a concise summary of the results of the entire project including the complete recommended modernization master plan subdivided by plant and by ammo category. Refs 2 to 4, with appendices, supply modernization master plans by ammo category together with the detailed advanced technology studies and other applicable background material. Refs 5 thru 25 present the modernization master plan for a GOCO plant with applicable analyses and background material. An appendix bound with each report includes P-15 summary sheets
and economic analyses for recommended production facility projects. Refs 26 to 32, bound separately in seven parts, report on the results of the LAP model line studies on specific end items. Refs 33 & 34 contain material on integration of the modernization master plan, feasibility study for economic model, and priority system.

Written by S. M. KAYE


Modified TNT. After WWI, a considerable quantity of Trojan grenade powd that had been spoiled by moisture, was available for use. It consisted of nitrostarch, Na nitrate, Amm nitrate, and a small quantity of oils. In order to utilize the powd, an equal amt of TNT was added, and the resulting mixt designated “modified TNT” was found to be an efficient expl. It was used as a commercial blasting expl. See Munroe-Neumann Effect, Vol 4, 444-R

Refs: 1) J.J. O’Connor, Ordn 37, 171 (1952) 2) OrTechTerm (1962), 197-L

Mohaupt Effect. The effect of a metal liner introduced in a shaped charge to increase penetration. Generally incorporated in high expl anti-tank (HEAT) ammo. See Munroe-Neumann Effect, Vol 4, 444-R

Refs: 1) J.J. O’Connor, Ordn 37, 171 (1952) 2) OrTechTerm (1962), 197-L

Moiesson Number (Nombre de Moisson in Fr). The Fr ballistician M.L. Gabeaud (Ref 1) claimed that the so-called Nombre de Mach (Mach number) should be called the Nombre de Moisson because it was the Fr Gen Moisson who first proposed the equation in 1883, four years before Mach. Gabeaud also stated that the Rus ballistician Gen Mayevski, in his work “Traité de Balistique Extérieure”, Gauthiers-Villars, Paris (1872), gave a somewhat similar equation for the detm of the resistance of air at the vel of sound, for round and elongated projectiles

Moisture. The effect of moisture on expls, prop- 
plnts and pyrots can be deleterious in terms of 
reliability, efficiency and safety. This unwanted 
ingredient can add uncertainty and possible 
hazard in the manuf, storage and eventual use 
of ammo. Moisture adds to the costs of ammo in 
many ways. These include less effective material 
being available per unit volume, with concomi-
tant increases in malfunction rate, curtailed 
shelf life because of structural failures occasioned 
by moisture-generated chem reaction products, 
and the cost of many investigations undertaken 
to understand and prevent effects (Expls: Refs 
6, 8, 11, 12, 15, 17, 21, 26, 28, 31, 34, 35, 39, 
40, 41, 43, 44, 46, 48, 52 & 54; Propilnts: 
Refs 9, 13, 16, 19, 21, 23, 27, 29, 37 & 53; 
Pyrots: Refs 5, 7, 10, 14, 18, 20, 23, 24, 28, 30 
& 38) 

Moisture exists in energetic materials pri-
marily because of the procedures used in their 
manuf. Since many of these materials are hygr- 
ous, they absorb moisture from the atm on site when 
they are prepd. In addition, w may be added for 
either safety considerations or as an economical 
solv in prodn procedures. Examples of these 
moisture sources include shell loading operations, 
which are performed using steam-heated faciliti-
es and cold w cooling jackets. The latter are 
used in many stages of expl and propilnt manuf. 
They condense atmospheric moisture onto their 
cold surfaces, some of which enters the mixt-
being processed, resulting typically in delayed 
expl gelation (Ref 34), undependable deton 
phenomena (Refs 26, 46, 48 & 54), or ballistic 
uncertainties with propilnts (Refs 13 & 27). 
Moisture can also permeate energetic materials 
during storage of ammo contg them (Refs 16, 
19, 37, 50, 53 & 59) 

Illustrations of the deleterious effects of 
moisture on the manuf, storage and performance 
of individual classes of energetic materials will 
now be considered 

Effect of Moisture on Explosives: Expls are the 
only energetic materials which can exist in 
useable form as a w slurry. These materials do 
not meet Mil specifications, however, they are 
commercially available and are used as gels in 
mining operations (Refs 35, 36, 43 & 44) 

The immediate effect of large amounts of mois-
ture on conventional Mil (and commercial) dry 
expls is to prevent deton. In Engl, to safely store 
many expls, the use of w wet materials is advan-
taged. Of course, a drying process must be used 
to make the expl useable and efficient. In this 
connection, to accurately determine the amnt of 
w required to prevent the accidental deton of 
expls, the Lonestone Cartridge Case Test was 
evolved (Ref 54). Presented below are results 
from this work, the data being obtained from 
plots of %w added to the dry expl vs the base wt 
of the expl plus added w, on attempting deton of 
the mixt. The plotted data resulted in sig-
moid-shaped curves which clearly define the 
minimum w content necessary for non-deton 

Table 1 
Minimum % of Water Required for 
Non-Detonation When Subjected to 
Contact Impulse from a Detonator 

<table>
<thead>
<tr>
<th>Explosive</th>
<th>% Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN</td>
<td>165</td>
</tr>
<tr>
<td>RDX</td>
<td>60</td>
</tr>
<tr>
<td>Tetryl, Gr I, cryst</td>
<td>60</td>
</tr>
<tr>
<td>1,3,5 Trinitrobenzene</td>
<td>55</td>
</tr>
<tr>
<td>RDX/TNT 80/20</td>
<td>48</td>
</tr>
<tr>
<td>Strontium picrate</td>
<td>31</td>
</tr>
<tr>
<td>2,4,6 Trinitrobenzoic acid</td>
<td>28</td>
</tr>
<tr>
<td>Picric Acid</td>
<td>26</td>
</tr>
<tr>
<td>TNT, cryst</td>
<td>20</td>
</tr>
<tr>
<td>Ammonium picrate</td>
<td>8</td>
</tr>
<tr>
<td>Gunpowder, mealed</td>
<td>7</td>
</tr>
<tr>
<td>Nitroguanidine</td>
<td>6</td>
</tr>
<tr>
<td>2,4 Dinitrophenol</td>
<td>4</td>
</tr>
<tr>
<td>Sodium 2,4 dinitrophenate</td>
<td>0</td>
</tr>
</tbody>
</table>

The work of Avrani et al on the impact sensy 
of Lead Azide-water (LA-w) mixts contg various 
expls and drying agents, conducted with the 
standard PicArsn impact test app, is of interest. 
It was found that under confined conditions, 
LA mixts contg up to 28% w are more sensitive 
than dry LA mixts, while in unconfined tests, 
the reverse is evident (Refs 39, 40 & 41). This 
study, as a corollary to the Lonestone test work, 
is indicative of the uncertainties inherent in 
expl initiation when w is present 

Small amts of moisture can also affect expl 
performance. As little as 0.5% can cause un-
predictable deton initiation and randomly 
variable deton vels, which could defeat the ef-
ficient use of an expl in, for example, a shaped 
charge application (Ref 26). See also Vol 4, 
D347-L & D356-R
On long term storage, moisture can cause undesirable chem reactions such as the formation of nitric acid, which can react with such metals as Al, Mg, Fe, Cu, etc., to yield H₂. The H₂, in turn, in redox reactions with both metals and org chemicals present can form shock sensitive comps (Refs 6, 11, 12, 15, 17 & 26). In addition, H₂ is extremely sensitive to spark initiation, and can cause premature detonons when ammo is being handled, is in-tube during launch, or is being steam-cleaned for reloading purposes. A parallel reaction involves the release of NH₃, which can combine with metals such as Cu in the presence of nitrates to form such extremely shock sensitive comps as tetramino cupric nitrate (Ref 17). To obviate these effects, desiccants such as silica gel may be added to the extent of 0.5% (Ref 12).

Moisture can also result in undesirable dimensional changes occurring in AN-K nitrate based exps, caused by changing crystal habit on thermal cycling. The physical stresses produced may cause stress failures of their containers (Refs 26 & 32).

**Effect of Moisture on Propellants.** The effects of the addition of 0.1% moisture on the performance of small arms propnlnt is shown below (Ref 13):

<table>
<thead>
<tr>
<th>Cartridge</th>
<th>Additional Charge (%) Required to Maintain Constant Velocity</th>
<th>Change in Velocity (%) for Constant Charge Weight</th>
<th>Change in Pressure (%) for Constant Charge Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single Base</td>
<td>Double Base</td>
<td>Single Base</td>
</tr>
<tr>
<td>Cal .50 AP</td>
<td>1.06</td>
<td>0.85</td>
<td>-0.70</td>
</tr>
<tr>
<td>Cal .30 Ball</td>
<td>0.64</td>
<td>-</td>
<td>-0.60</td>
</tr>
<tr>
<td>Cal .30 AP</td>
<td>0.56</td>
<td>0.56</td>
<td>-0.55</td>
</tr>
<tr>
<td>Cal .45 Ball</td>
<td>1.00</td>
<td>-</td>
<td>-0.55</td>
</tr>
</tbody>
</table>

The deterioration of propnlnt charge increment bags because of moisture has been reported (Refs 16, 19 & 53). Since each bag contains a charge necessary to obtain a finite range for a finite prop, moisture-caused deterioration of the bag with associated propnlnt degradation can defeat the increment’s purpose and produce an unpredictable, erratic round.

The effect of moisture on felted combustible cartridge cases includes ignition delay, and out-of-phase or low peak pressures, all contributing to round inaccuracy (Ref 37). Temp cycling of this item can trigger an excess of moisture in the casing matrix will lead to case embrittlement, cracking and eventual case rupture. This effect has led to the development of protective coatings and seals (Refs 19, 23 & 37).

Small arms ammo can be so severely affected by moisture that a special indicating lacquer was developed for 20mm rounds which changes color from grey to black on w xposure (Ref 59). **Effect of Moisture on Pyrotechnics:** Pyrot formulations usually contain finely powdered metal fuels such as Mg, Al, Fe, Cu, etc., all of which can react with moisture to yield H₂. This effect has been dubbed “gassing” in pyrot circles, and is the major problem associated with the storage of hermetically sealed ammo of this class. The pyrot charges so affected become deton sensitive, and are generally unreliable as to burning rate and illumination. An associated effect of “gassing” is the deformation and rupture of ammo casings, making the items non-serviceable. Many programs have been initiated to circumvent these effects, and have included the use of dichromate, resin and wax coatings for the metal particles. The inclusion of drying
agents in pyrot formulations, careful pre-drying of ingredients and post-processing drying of loaded items, as well as hermetic sealing of end-item casings have been attempted (Refs 5, 7, 10, 14, 18, 20, 23, 24, 30 & 38)

The salts of Na, Ba and Sr, used as oxidants and to impart appropriate flame colors, are water soluble. Excessive moisture content (over 0.5%) is deleterious in terms of light intensity, color saturation and burning duration. BlkPdr, a widely used ignition source and flame transfer agent, absorbs moisture and deteriorates rapidly. Many instances of pyrot "no-fire" incidents have been found to be the result of such deterioration (Refs 10, 18, 21 & 38)

**Moisture, Analytical Procedures.** Various quantitative procedures have been developed ranging from simple oven drying thru sophisticated instrumental methods (Expts: Refs 31, 33, 42, 47, 52, 56, 57, 60 & 62; Proplnts: Refs 25, 28, 29, 49, 51 & 55; Pyrots: 30 & 38)

Many procedures have already been described in this Encycl, and are listed below:

Encycl 6, D1620-L to D1622-R (Moisture by Distillation Method); Ibid, D1622-R to D1628-L (Moisture by Karl Fischer Method); Encycl 6, E158-L to E160-R (Water by Karl Fischer Method); Ibid, E162-R to E164-R (Ethanol, Ether and Water Determinations in Single Base Propellants by Gas Chromatographic Method); Ibid, E164-R to E169-R (Total Volatiles and Moisture Using the Vacuum Oven Method); Ibid, E170 (Electrolytic Hygrometer Method); Ibid, E171-L to E172-L (Moisture Determination in Propellants and Explosives by Distillation Method); Ibid, E172-L to E173-L (Moisture Determination in Propellants and Explosives by the Karl Fischer Method)

Encycl 6, E173-L details a literature method for detg w in NC and proplnts thru the use of dry K carbonate pumice to absorb w in a gravimetric procedure. Encycl 6, E176-R describes a differential d measurement of the solvents used in proplnt maruf for the det of alc, eth & w (Ref 2). Other old gravimetric methods are given in Refs 1, 3 & 4

A modern version of the oven heating method is the Mytron FAB-1 moisture tester, in use at Waltham Abbey, Sussex, Eng., for detg moisture in proplnts (Ref 55). It consists of a hot air oven containing a motor driven turntable with numbered spaces for 10 circular flat Al dishes. Below the oven compartment is a simple beam balance, so arranged that when the beam is moved from rest onto its knife edges, the rotation of the turntable is stopped and the wt of the dish immediately above the balance is recorded on a scale that shows % moisture lost (a 10g sample being specified). The range of the balance is 0 to 22% moisture

Ref 58 discusses the application of electronic instrumentation to moisture measurement. Procedures amenable to use for energetic materials include:

**Capacitive Sensors.** This device usually consists of a capacitor which is formed either from two concentric cylinders or from a pair of parallel plates. The solid sample to be analyzed for moisture content is passed between these plates. Since w has a large dielectric constant, the w content of the sample causes a significant change in the dielectric constant of the solid, which is measured using bridge or frequency techniques. To obtain the % of moisture directly, a calibration curve is first constructed which relates % moisture in the solid to capacitance. A drawback inherent in this method is the dependence of the dielectric constant on factors other than moisture content, such as density, particle size and packing. Ref 61 describes a Capacitance Moisture Analyzer (CMA) capable of providing moisture analyses of LA with a precision of ± 0.17% in samples containing a max of 0.5% w

**Neutron Measurements.** The interaction of neutrons has been used on a laboratory basis to measure low concentrations of moisture in powd expls and other energetic materials. The approach is based on the phenomena that fast neutrons, on passing thru materials of high scattering and stopping power, are slowed down to slow or thermal energies. The fractional loss in energy when a neutron collides with an atom is greatest for the H atom. Thus, by passing a beam of fast neutrons thru a series of samples of the same material, but with varying moisture contents, a relationship is observed between moisture content and measured thermal neutron intensity. Using a small radioisotope fast neutron source and a lithium iodide thermal neutron detector, this neutron
moderation technique was applied to the measurement of moisture content in AN, K nitrate, BlkPdr, K perchlorate and NC in the range from 0.01 to 10 wt % (Refs 42 & 57). For additional details see Encycl 8 under Nuclear Applications.

**Nuclear Magnetic Resonance.** This transient NMR technique, developed by the Southwest Research Institute, permits moisture in BlkPdr to be measured without weighing by sampling the amplitude of the free induction magnetic decay at two points in time. Amplitude measurements of the BlkPdr signal shape enables one to obtain signals linearly related to the solid material (the dry wt of the sample) and liq (w) signals respectively. Moisture levels in the range 0.2 to 1.0% can be measured with an accuracy of ± 5.5%. The accuracy with which a measurement can be repeated is 1.0% of the quantity measured (Ref 47).

**Infrared Spectroscopy.** A device known as OMA, an acronym for Optical Moisture Analyzer, has been used to determine moisture content in non-metallic cartridge cases and certain fine-grained propellants (Ref 51). The operating principle of the OMA depends on the utilization of discrete portions of the electromagnetic spectrum. The "near" infra-red region, between 0.7–2.5 microns permits the use of relatively simple optical systems and includes a strong w-absorbent band at 1.93 microns so that moisture content may be determined by measuring the attenuation, at this wavelength, of an infra-red beam reflected from the surface of a sample. A reference beam (at a wavelength unaffected by moisture) is used to compensate for variations in reflectance and dispersion at the sample surface. Since both beams are responsive to these factors, the difference in attenuation represents the effect of moisture only.

For this instrument to be applicable, a sample material must satisfy the following requirements: Its surface must be reflective enough to activate the PbS detector; it must be thermally non-conductive so that the infra-red energy will be reflected rather than transmitted; it must have a moisture content at the surface that is representative of the total moisture; and, it must not be so thin that incident radiation either passes thru the sample or is reflected by a backing material or a sample container.

Written by H. L. HERMAN

Knapp, “Investigations of Torpedo Igniter Mark VI, Models 2, 3 and 4”, PATR 2180 (1955)
59. B.W. Brodman & M.J. Ennis, "Moisture Indicating Lacquer for 20mm Ammunition", Frankford
Ars MR M-73-20-1 (1973) 60. Anon, "Explosive Composition A-5", US Mil Spec MIL-E-
14970B (1974) 61. A.A. Nativo, "Instrumental Moisture Analysis of Initiating Explosives
for Use in the Modernized Detonator Backline", PATR 4727 (1974)

Molasses (Treacle). There are several types of molasses, differing as to method of prep and
source; whether from beet root or cane sugar.
In the beet sugar industry, molasses represents
the final mother liquor, obtained after concn of
the beet juice and crystallization. Such molasses cont about 50% sucrose,
with only traces of reducing sugars. In the cane
sugar industries, molasses is a syrupy mother
liquor left after the sugar has been removed by
centrifugation. If only one
crop of crystals is removed, the molasses is known as "first molasses"; if two crops, as "second
molasses", etc. The final mother liquor, from
which no more sugar can be extd by usual
factory practice, is called "blackstrap" and cont
about 30% sucrose and 20% reducing sugars
(Refs 2, 3)

Korbonits (Ref 1), commenting on a spontaneouse ignition in a molasses tank, recommended
that excessive foaming be avoided. He stated
that molasses should be poured slowly into tanks,
stirring must be done slowly, and manholes
should be left open until the molasses is cooled.

Molasses in nitrat form has also been used in
some expls (see below)
Refs: 1) A. Korbonits, Mezőgazdaság és Ipar
3, No 9, 25-28 (1949) & CA 46, 283 (1952)
2) Kirk & Othmer 13, 613-33 (1967)
3) CondChemDict (1971), 591-L

Nitrat Molasses. The nitrat of molasses
produces liq and solid nitrates of variable N
content and expl props. They were used as
constituents of Keil's exps and in Martinsen's
Powder (qv)
Ref: Daniel (1902), 562-3

Molex Explosives. According to Hopper (Ref
2), Molex no's 2 & 3 are physical mixts of AN
52-84, K perchlorate 0-20, DNT oil 7-12,
baked cork 1-10, Al powd 5-7 & Ca carbonate
1%. They exhibited satisfactory sensitivity to
impact, friction, flame & initiation, and had excel
lent stability. Phillips (Ref 4) reported on tests
of Molex "B" and "BB", manufd by the
National Explosives Co. They are described as
physical mixts of AN 80.77-85.06, flake Al
6.02-6.10, DNT oil 4.32-5.84, activated cork
2.55-4.47, Ca stearate 1.10-1.99 and Ca carbonate
0.83-0.95%. They were shown to be
stable, to have fairly high brisance, but to be
sufficiently sensitive to expl in the rifle bullet
impact test. Byers (Refs 1 & 3) describes
blasting expls similar in compn
Refs: 1) L.S. Byers, USP 2079105 (1937) &
CA 31,4500 (1937) 2) J.D. Hopper, PATR
938, "Test of Explosive "Molex"", (1938)
3) L.S. Byers, USP 2136205 (1939) & CA 33,
1500 (1939) 4) A.J. Phillips, "Tests of Molex
Explosive 'B' and 'BB' ", PATR 1094 (1941)

Monachit. A Ger blasting expl also known as
Vigorit. Monachit I cont AN 81, trinitroxylene
(TNX) 13, K nitrate 5, and flour 1%. Monachit
II cont AN 64, TNX 12, K nitrate plus Na
nitrate 3, K chloride 19, charcoal 1, colloid
ion 1%. Monachit II has a limit charge of
more than 500g. Its vel of deton at d 1.20
g/cc is about 4800m/sec, while at d 1.56g/cc
it falls to 1780m/sec
Refs: 1) H. Kast, SS 8, 136 (1913) 2)
Marshall 1, 392 (1917) 3) Marshall, Dict
(1920), 63

Monakay Explosive. Dyn consisting of NG ab-
sorbed by a mixt, in equal wts, of Na nitrate,
ashe, carbon bk, earth and borax, to which
which was added 12.5% kerosene
Ref: Daniel (1902), 442

Monarkite. Brit permitted mining expl contg
typically NG 12.0, AN 4.97, Na chloride 24.5,
Na nitrate 7.5, starch 4.0, mineral jelly 2.0,
and colloidion cotton 0.3%. Its charge limit is
26oz, and power by BaldPend is 2.61 inches
Monoacyl Glycerol Nitrates. Formed by reacting in the liquid phase at temps as high as 120°, a mix of glycide nitrate and an aliphatic carboxylic acid of the benzene series such as benzoic acid, with FeCl₃ as catalyst. They were recommended as additives for NG, or like expls, to lower their freezing points
Ref: H. Jacobi & W. Flemming, USP 2302324 (1942) & CA 37, 1412 (1943)

Monobels. Brit permitted mining expls made by Nobel's Explosives Co (Refs 1, 2 & 3):

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monobel No</td>
</tr>
<tr>
<td>NG, %</td>
</tr>
<tr>
<td>AN, %</td>
</tr>
<tr>
<td>Woodmeal, %</td>
</tr>
<tr>
<td>Na chloride, %</td>
</tr>
<tr>
<td>K chloride, %</td>
</tr>
<tr>
<td>Mg carbonate, %</td>
</tr>
<tr>
<td>Limit charge, oz</td>
</tr>
<tr>
<td>Power (swing of Bulpend), inches</td>
</tr>
</tbody>
</table>

The duPont Co manufd under this name, low velocity permissible expls in six grades, AA, A, B, C, D and E, based upon velocity and cartridge count. As a rule, these grades are used in operations where coarse coal is desired (Refs 4 & 5)

Ref: 1) Marshall 1, 396 (1917) & 3, 120 (1932)
2) Marshall, Dict (1920), 64
3) Davis (1943), 342 & 351
4) Blasters' Hdb (1950), 67
5) Cook (1958), 10

Mono-Oil. (Commercial mono nitro toluene). Mixt of about 62% ortho-, 34% para-, and 4% meta-nitrotoluene. Yel oil with pungent odor, d 1.16g/cc; distills between 220°-240°. It is used in low-freeze Dynamites, as a plasticizer for NC, and in blasting expls in combination with chlorates or nitrates. Such plastic expls have the desirable property of completely filling the bore hole by using only a light press. The oily nitro compound also serves as a protection against dampness, and it has the advantage of being an active ingredient in comparison with paraffins and greases which have previously been used as plasticizers
Ref: Bebie (1943), 103-4

Monopropellant. The common name for any single, stable fluid which cont an oxidizing agent and combustible material that can undergo an exothermic reaction to release heat for conversion to propulsive thrust in a typical rocket thrust-chamber assembly. It requires no auxiliary oxidizer for the release of its thermochemical energy, although it may require a solid or liq catalyst. The solid catalyst can be said pellets previously soaked in a liq catalyst. Although the use of a liq catalyst to break down the monopropellant actually constitutes a second working fluid, it has not become the practice to name these systems as bipropellant rocket power plants because the catalyst does not cont either the oxid or the fuel (Ref 4)

A partial list of monopropellants that have been tested and applied to the production of rocket thrust includes coned high strength hydrogen peroxide (85% or above), ethylene oxide, ethyl nitrate, methyl nitrate, hydrazine, propane, nitromethane, and n-propyl nitrate (Refs 2 & 6)

The burning of a monopropellant resembles the burning of a fuel in an internal combstn engine because of the formation of fine droplets, their vaporization and their burning, although no air is introduced as in a carburetor. Also, since the combstn chamber is a straight tube, there is no specific sepn between the droplets and the final gaseous combstn products. As a result, during equil burning, liq is being injected as a spray at one end of the chamber, vaporized further down the tube, ignited and completely decompd just prior to entering the exhaust nozzle. Because the flow rates are high and there is a considerable amt of turbulence, sharp definition of the various reactions is not possible. Nevertheless, there is a specific area which can be characterized as the “flame front”. The liq and gaseous phase chemical reactions, and the interaction between such physical reactions as droplet formation, evap, and diffusion, prevent the selection of any one process as the rate-controlling one. Experience has shown that each monopropellant requires a specific type of injector and a specific chamber length for a given mass flow rate in order to ef-
fect complete decompn of the propInt (Ref 3)

Liq monopropants are inherently unstable and consequently behave in an unpredictable manner. One of a number of reasons why this class of propInts is not used more frequently is that they have a tendency to change over from an actual burning rate to a detont velocity. When this occurs in the inlet lines, the detont is transmitted back to the propInt tank with disastrous results (Ref 3)

The term monopropLang has also been applied to solids, where a solid monopropLang is defined as a single physical phase comprising both oxidizing and fuel elements. These include many chemicals used as Mil high explosives, as the thermochemistry of propants is essentially the same as that for HE's. The difference between combstn and detont of a cryst monopropLang is merely a difference in reaction rate (Ref 1). Except for primary expls which can detont on burning, these chemicals will burn quietly when ignited. They will detont only under the influence of a mechanical shock of severity far greater than can be found in a rocket chamber. The physical and ballistic props of NGu, RDX, HMX, PETN, Amm nitrate, and Amm perchlorate are detailed in Ref 5


Monetriethyl Lead Azoaminotetrazole. See Azoaminotetrazole, listed under Tetrazoles

Montan Wax (Lignite wax). White, hard earth wax; crude product, dark brown, mp 80–90°. Obtained by countercurrent extrn of lignite. Sol in CCl₄, benz & chl; insol in w. It is combustible & nontoxic. Has been used extensively in Ger for coating particles of expls such as PETN & RDX, in order to reduce their sensitivity to impact and friction

Ref: CondChemDict (1971), 595–R

Moorp Propellant. A series of rocket proplnts submitted to PicArsn for evaluation in 1949. They consisted of an oxidizer (such as K perchlorate) 70, and a cured rubber hydrocarbon plus accelerators, 30%. Although the examined samples proved to possess desirable props for rocket propIo use, their thermal stability was poor and their press exponent undesirably high. It was concluded that further work was required on the method of prepn to eliminate these defects


Morse's Powder (or Explosive). Inexpensive expl mixts, invented by C.A. Morse in 1880, consisting of NG and resin (colophony, copal, shellac, sandarac), with or without the addition of a nitrate or chloride. The ingredients were dist in a common solvent, such as methanol, grained as the solvent distd off. Typical examples are: 1) NG 25, rosin 75% (mixed with 50p methanol); 2) NG 10, rosin 22, K nitrate 68% (mixed with 20p methanol)

Refs: 1) Daniel (1902), 443 2) Van Gelder & Schlatter (1927), 658

Mortars. See under Cannon, Vol 2, C27–R–C28–L. Addnl updated references are given below


Mortar, Ballistic. See Ballistic Mortar Test, Vol 2, B6-R

Mortier and Sandon. Patented in 1897 the following cannon powd: K nitrate 65, trinitroresol 25, charcoal 9 & stearic acid 1%  
Ref: Daniel (1902), 443

Moss. Proposed as an absorbent for NG in Dyn  
Ref: C.O. Black & W.A. Moore, USP 1713816 (1921) & CA 23, 3576 (1929)

Motorite. An expl mixt, consisting of NG 70 and guncotton 30%, which was proposed in the USA for use as a fuel for the propulsion of torpedoes and torpedo boats  
Ref: H. Maxim, CA 3, 375 (1909)

Motors Activated by Explosives (Moteurs à explosifs). Huygens, in 1678, first proposed construction of a motor in which the explns of BlkPdr were to be utilized for motive force. A similar concept was proposed in 1680 by Hautefeuille, and the first motor of this type was actually constructed later by Papin. Other motors were built in the 18th and 19th centuries, notably those of Gras, Renoir, Hureau de Ville-neuve and Penaud, Wolf and Pietzcker, Hawkins, von Ruckterschell, etc. However, none of these could compete economically with steam engines existing at the time, even though they were lighter than steam engines of corresponding horsepower  
Ref: Daniel (1902), 444

Mowbray, G.M. (1814–1891). Brit-American chemist who arrived from Engl about 1855, and was one of the first to manuf NG. His product was used in the construction of the Hoosac tunnel. He later did valuable work in the development of Zylonite (qv) and also expd with propint powd  
Refs: 1) Daniel (1902), 445  2) Van Gelder & Schlatter (1927), 375

MOX Explosives. Expl mixts contg a HE plus powd metal and an oxidizing agent. They were developed beginning in 1950 by National Northern, technical division of the National Fireworks Ordnance Corp, West Hanover, Mass, USA, and were used in small cal antiaircraft projectiles (Refs 1, 2, 3, 4, 5, 7 & 11). MOX formulations and more important props are given below (Ref 12):
# Table 1

<table>
<thead>
<tr>
<th>Composition, %</th>
<th>MOX</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$ClO$_4$</td>
<td>35.0</td>
<td>35.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNO$_3$</td>
<td></td>
<td></td>
<td></td>
<td>18.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(NO$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>Al, atomized</td>
<td>26.2</td>
<td>52.4</td>
<td>50.0</td>
<td>50.0</td>
<td>49.2</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.7</td>
</tr>
<tr>
<td>Mg, atomized</td>
<td>26.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other ingredients *</td>
<td>9.7</td>
<td>9.7</td>
<td>32.0</td>
<td>32.0</td>
<td>29.6</td>
<td></td>
</tr>
<tr>
<td>Ca stearate</td>
<td>1.9</td>
<td>1.9</td>
<td>2.0$^a$</td>
<td>2.0$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite, artificial</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0$^a$</td>
<td>1.0$^a$</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>OB to CO$_2$, %</td>
<td></td>
<td></td>
<td></td>
<td>44</td>
<td>49</td>
<td>52</td>
</tr>
<tr>
<td>OB to CO, %</td>
<td></td>
<td></td>
<td></td>
<td>37</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>Q$_c$, cal/g</td>
<td>4087</td>
<td>4484</td>
<td>4331</td>
<td>4392</td>
<td>4293</td>
<td></td>
</tr>
<tr>
<td>Q$_b$, cal/g</td>
<td>2087</td>
<td>1472</td>
<td>980</td>
<td>709</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>Gas vol, cc/g</td>
<td>212</td>
<td>221</td>
<td>232</td>
<td>208</td>
<td>204</td>
<td></td>
</tr>
<tr>
<td>Activation energy, kcal/mole</td>
<td>12.5</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PicArsn Impact Test, inches</td>
<td>13</td>
<td>12</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Expln temp, 5 sec, °C</td>
<td>285</td>
<td>375</td>
<td>540</td>
<td>610</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>Sand Test Value</td>
<td>10.6</td>
<td>11.5</td>
<td>33.2</td>
<td>33.6</td>
<td>10.8</td>
<td></td>
</tr>
</tbody>
</table>

100$^o$ Heat Test:

- % Loss, 1st 48 hrs: 0.10, 0.27, 0.35, 0.22, 0.00
- % Loss, 2nd 48 hrs: 0.01, 0.12, 0.13, 0.12, 0.00
- Explosion in 100 hrs: None, None, None, None, None

* (MOX-1) Tetryl
(MOX-2B) 5.8% RDX & 3.9% TNT coated on NH$_4$ClO$_4$
(MOX-3B) 29.1% RDX, 0.9% wax & 2.0% TNT
(MOX-4B) same as 3B
(MOX-6B) 28.7% RDX coated, 0.9% wax

$^a$ Percent added

Blast measurements made with MOX-2B are given relative to TNT in Ref 12:

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>Bare Charge in Air</th>
<th>Cased Charge in Air$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EW*</td>
<td>EV*</td>
</tr>
<tr>
<td>Peak Pressure</td>
<td>1.02</td>
<td>1.34</td>
</tr>
<tr>
<td>Impulse</td>
<td>1.08</td>
<td>1.41</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.96</td>
<td>1.96</td>
</tr>
</tbody>
</table>

* EW, equiv wt as compared to TNT
* EV, equiv vol as compared to TNT
** strong, paper base phenolic case

### Preparation of MOX Explosives

The various ingredients used in the prep of MOX expls are coated separately as follows:
Dichromated Atomized Aluminum. 75g of chemically pure grade Na dichromate is dissolved in 1500ml of $w$ at 100$^o$ under mechanical agitation. 600g of atom Al powd is added gradually (2-3 mins) and stirring is continued for 0.5 hr. The dichromated material is filtered, washed with $w$ (15-20 times) until the washings show only a sl cloudiness with Ag nitrate. The w
wet prod is then dried at 50°, hand-rolled to reduce any agglomerates, and blended before use Wax-Coated RDX. 18g of molten Be Square Special Wax (manufacturers’ 180° to 185°F grade amber) is added to 582g of finely divided RDX (w pptd from acet soln) in a w slurry under mechanical agitation. The temp of the wax-RDX slurry is maintained above the mp of the wax (about 90°), and the stirring is contd for 0.5 hr. After cooling to 50°, the wax-coated RDX is recovered by filtrn and air dried. The RDX thus coated and presumed to be 3% waxed RDX or a 97/3 RDX/wax mixt, is hand rolled to crush agglomerates and hand blended before use

*TNT-Coated Barium Nitrate. 30g of TNT in alc soln is added to 270g of Ba nitrate in an alc slurry under agitation. The temp of the mixt is maintained at 80° and stirring is contd until most of the alc is evapd. The coated material is spread in a thin layer and air dried overnight. The Ba nitrate thus coated with 10% TNT is reduced to an intimate mixt by hand rolling and blending before use

*TNT-Coated Potassium Nitrate. Prepd by the same procedure used for coating Ba nitrate RDX/TNT Coated Ammonium Perchlorate. The Amm perchlorate is coated by dissolving the appropriate wts of RDX & TNT in hot alc. After adding the Amm perchlorate, the slurry is stirred until most of the solv is evapd. The treated material is spread on a tray to dry overnight. Agglomerates formed during the process are crushed by hand rolling and blending the mixt before use

*TNT Coated RDX. 60g of molten TNT are added to a w slurry of 540g of finely divided RDX (w ppt from acet soln) under mechanical agitation. The temp of the TNT-RDX slurry is maintained at about 90° and stirring is contd for 0.5 hr. After cooling to about 50°, the TNT-coated RDX is recovered by filtrn. The RDX thus treated, and presumed to be 10% coated or a 90/10 RDX/TNT mixt, is further blended by hand after rolling to crush any aggregates formed during the process

The MOX expl mixts are prepd by blending the appropriate wts of the dry ingredients in a twin-shell blender for at least 30 mins


MSX. Code name for 1-Acetoxo-2,4,6-trinitro-2,4,6-triazahexane. Described in Vol 1, A53-L
MS-80 Blasting Agents. Dow Chemical Co. products consisting of soft, silvery gels contg AN and Al particles. Five different strengths are available, ranging from 1.4 to 6.0 times the blasting power of AN-fuel oil expls. Their blasting power is det by the Al content, which ranges from 5 to 30% by wt. Although they contain no TNT, NG or other HE sensitizer, Dow claims that they outperform slurries contg Al plus TNT.

Ref: Anon, C&EN 42, 29-30 (April 27, 1964)

MTTC. A Fr expl contg PA 55, TNT 35 and TN-m-cresol 10%, melting below 100°, used for cast loading of HE projectiles. DNPH can be substituted for TN-m-cresol (Ref 4)

Refs: 1) Pascal (1930), 214-17 2) Vennin, Burlot & Lécorché (1932), 457 3) Davis (1943), 166 4) Bebie (1943), 104

MTX. A Fr expl used during WW1 consisting of PA, TNT and TN-m-xylene. Pascal (Ref 1) gives its compn as PA 30, TNT 20 and TN-m-xylene 45%, while Vennin, Burlot & Lécorché (Ref 2) state the ratio as 55/35/10

Refs: 1) Pascal (1930), 213 2) Vennin, Burlot & Lécorché (1932), 457

MUCIC ACID AND DERIVATIVES

Mucic Acid (Galactaric acid, Galactosaccharic acid, Tetrahydroxyadipic acid, Saccharolactic acid, Schleimsaure (Ger).)

\[
\begin{align*}
\text{HO}_2\text{C} & - \text{C} - \text{C} - \text{C} - \text{CO}_2 \text{H} \\
\text{O} & \text{H} \quad \text{O} \\
\text{H} & \text{H} \\
\end{align*}
\]

mw 210.14, OB to CO\(_2\) = 68.53%, white prisms, dec about 255° when heated rapidly, 210° when heated slowly. Soln in 300p cold w, 60p boiling w, alkalies; practically insol in alc & eth. Prepn from oxidaion of lactose with dil nitric acid on heating (Ref 1)


Diazomucic Acid. N\(_3\)CO.(CHOH)\(_4\)CO.N\(_3\), mw 260.20, N 32.31%, OB to CO\(_2\) = 61.49%, microcryst, very sol in w. Prepd from mucic acid hydrazid and nitrous acid. It explodes on heating

Ref: Beil 3, 585 & (202)

Mucic Acid Trinitrate (Galactan Trinitrate).

\[
\begin{align*}
\text{CH}_2 & \text{O} \\
\text{CH} & \text{ON} \quad \text{O} \\
\text{CH}_2(\text{ONO}_2) & \text{CH} \\
\end{align*}
\]

mw 297.16, N 14.14%, OB to CO\(_2\) = 24.20%, cryst. Prepn from d-galactose and mixed acid (nitric/sulfuric). Brissage by sand test; 0.4g (13.45% N) crushes 42g of sand. Impact sensitivity is the same as Tetryl. The material is very unstable; however, this may be because of impurities

Refs: 1) Beil, not found 2) Blatt, OSRD 2014 (1944)

Silver Mucic Acid Diamide.

\[
\text{HO}_2\text{C}.\text{N} \text{Ag}.\text{CHOH}.\text{CHOH}.\text{Ag} \cdot \text{CO}_2 \text{H}
\]

mw 435.90, N 6.43%, OB to CO\(_2\) = 33.04%, gelatinous ppt. Prepn from diazomucic acid by heating in w and reacting the product in NaOH soln with Ag nitrate. The compound expls on heating

Ref: Beil 3, (202)

Mudcapping. Rocks and boulders buried either partially or completely underground can be successfully removed by operations such as “blockholing” or “snake-holing” (qv). If, however, the boulder or rock is at ground level or only slightly imbedded, it may be broken up by positioning a fused expl charge (usually 1-3 lbs per cubic yard of boulder) atop the boulder, plastering it over with mud and firing. The mud covering, usually 3-4 inches thick, should be free from stones, as the blast would propel them as projectiles.


Mullerites. Smokeless NC shot-gun powds
manufd by Müller et Cie in Belg, contg no inorganic salts
Refs: 1) Daniel (1902), 446  2) Barnett (1919), 87  3) Marshall, Dict (1920), 64

Multiperforated Propellant Grains. See Cannon Propellant or Cannon Powder in Vol 2, C30–31, & Grains of Smokeless Proplnts in Vol 6, G123

Mundell or Pertuiset Powder. Compn proposed by de Fleuron in 1867 to be used in lieu of BKPdr. It consisted of K chlorate 63.49, sulfur 31.74, BKPdr 4.14 & animal charcoal 0.63%
Ref: Daniel (1902), 447 & 610

Munroe, Charles Edward (1849–1938). Leader in the development of expls in the USA. Inventor of the first American smokeless powder, Indurite (qv), and discoverer of the Munroe Effect (See Detonation, Munroe-Neumann Effect (Or Shaped Charge Effect) in Vol 4, D442-R to D454-L). Professor of chemistry at the US Naval Academy, Annapolis, Md, 1874–1886; chemist at the Naval Torpedo Station and Naval War College, Newport, RI, 1886–1892; professor of chemistry at George Washington University, 1892–1917; and chief expls chemist of the US Bureau of Mines, 1919–1933. Author and co-author of numerous publications on expls
2) Anon, JACS News Ed 16, 647 (1938)
3) C.A. Browne, JACS 61, 731 (1939)
4) Davis (1943), 18–20

Muraour, Henri (1881–1954). Fr scientist, a specialist in expls (Ingénieur général des poudres) and ballistics. Published more than 200 papers from WWI thru 1952 (Ref 2) on expls, proplnts, combstn of proplnts, expl phenomena, anti-flash agents, purification of TNT, theory of expl reactions, etc, as well as a widely read book (Ref 1)
2) Anon, MAF 24, 586–608 (1950) & CA 46, 7329 (1952)
3) Anon, MAF 28, No 108 (1954) (Obituary)
The following references detail Muraour’s more important publications: 1) H. Muraour & G. Aunis, CR 192, 418–21 (1931) & CA 25, 2569 (1931) (Variations in \( f'\)Pdt with loading d for poudres B contg either vaseline or centra-lite) 2) H. Muraour & G. Aunis, CR 193, 1082–4 (1931) & CA 26, 1124 (1932) (Continuation of work in Ref 1) 3) H. Muraour & G. Aunis, CR 194, 1927–9 (1932) & CA 27, 190 (1933) (Influence of proplnt temp on variation of \( f'\)Pdt at different loading d’s) 4) H. Muraour & G. Aunis, CR 196, 478–80 (1933) & CA 27, 2301 (1933) (Laws of combstn of mixts of slow & fast burning proplnts are the same as for the slow burning proplnt alone, ie., if \( f'\)Pdt is plotted vs time, the values fall on the same straight line in both cases) 5) H. Muraour, BullFr 9, 511–16 (1942) & CA 37, 6526 (1943) (Rate of combstn of colloidal proplnts as a function of the press & temp of emitted gases) 6) H. Muraour, Chim&Ind(Paris) 47, 602–606 (1942) & CA 40, 2985 (1946) (Study of the validity of the relation \( V=\alpha+\beta d\) in combstn of proplnts) 7) H. Muraour, Chim&Ind(Paris) 48, 11–13 (1942) & CA 38, 4446 (1944) (Investigation of the change of \( f'\)Pdt with d of charge) 8) H. Muraour, Chim&Ind(Paris) 49, 253–4 (1943) & CA 39, 3161 (1945) (Influence of the variable “time” in the combstn of colloidal proplnts in a closed vessel) 9) H. Muraour, Chim&Ind(Paris) 49, 254–5 (1943) & CA 39, 3161 (1945) (Influence of geometric form of proplnt grains on the total effect of pseudo-radiation) 10) H. Muraour, Chim&Ind(Paris) 50, 105–08 & 168–72 (1943) & CA 39, 3161 (1945) & 40, 2986 (1946) (Relation between expl temp of a proplnt and its vel of combstn; experimental results) 11) H. Muraour & G. Aunis, CR 220, 198–9 (1945) & CA 40, 5252 (1946) (Variation in the rate of combstn of colloidal proplnts as a function of temp) 12) H. Muraour & G. Aunis, CR 225, 381–3 (1947) & CA 42, 2431 (1948) (Modification of a previously presented formula for the relation between the expl temp of a colloidal proplnt and its combstn vel; the new formula reads: \( V=0.13+0.54(T_p') / 1000 \), where \( V \) is burning rate and \( T_p' \) is the temp reached after NO has completely disappeared) 13) H. Muraour & G. Aunis, MAF 22, 133–70 (1948) & CA 44, 8659 (1950) (The press and covolume

Murtineddu Powder. A mixt patented in 1856 contg K or Na nitrates, sulfur, sawdust, dried horse dung, Na chloride and nitrated molasses Ref: Daniel (1902), 447

Mustard Gas (Yperite, 2,2′-Dichlorodiethyl sulfide). C₄H₈Cl₂S, mw 158.9, oily liq, bp 215–17⁰, d 1.28g/cc. A toxic agent first employed by Ger during WWI at Ypres in 1917. Its variants are still deployed for military use. Mustard and its modern derivatives are almost colorless but have a faint garlic or mustard smell if impure. It penetrates normal clothing, causing severe burns, and it inflames the eyes and irritates the lungs. Short exposure to an atm concn of one p in 100000 causes acute vomiting and fever. The effect is delayed so that an effective dose can be absorbed before the agent is detected. Modern derivatives, T, O and HN-3, are lethal in smaller doses. O causes incapacitating blisters after 3mgs are absorbed. No adequate treatment exists, and mustard is the most severe blistering agent in existence.


Muzzle. The end of the barrel of a gun from which the bullet or projectile emerges Ref: OrdTechTerm (1962), 199-R

Muzzle Brake. (Freins de bouche in Fr, Mündungsbrm in Ger). A cylindrical device with flanged or baffled surfaces which is attached to the muzzle of a gun, usually by threads, to offset a long or complete recoil of the gun when fired. The expanding proplnt gases strike the baffles, thus pushing the gun barrel forward. This action can shorten the actual recoil distance, or it may relieve an overloaded recoil system. The latter would occur when a conventional gun was deliberately overloaded to increase the projectile velocity.


Muzzle Flash or Muzzle Flame. Flame that appears at the muzzle of a gun when a projectile leaves the barrel. See Flash Reducing (or Anti-flash) Agents, Flash Reduction in Ger Projectiles, and Flash Reduction in Ger Proplnts, Vol 6, F96-L to F99-L Ref: OrdTechTerm (1962), 200-L

Muzzle Velocity (MV, Initial Velocity). The velocity at which a projectile leaves the muzzle of a gun, expressed either in m/sec or ft/sec. The moment the projectile emerges from the bore, its velocity starts to decrease because of air resistance. For this reason, the muzzle velocity is considered as the max velocity of a
projectile. Strictly speaking, however, this is not true, because the projectile might be slightly accelerated after emergence from the bore by expanding proplnt gases immediately after friction between the projectile and the bore has ceased. As it is very difficult to devin the velocity close to the muzzle, the usual practice is to measure it a short distance from the muzzle, eg, 78 ft, and then either to correct back to the muzzle for the retardation in flight (as is done for artillery ammo), or to take it as such (usually done for small arms ammo).

Muzzle velocities may either be calcd by means of equations, such as that of LeDuc (Ref 1, p 74) or detd experimentally thru use of chronographs (Refs 4 & 5).


MVT. Abbr for Methyl Vinyl Tetrazoles, described under Tetrazoles

Myrite. An expl contg a mixt of nitrogen dioxide and carbon bisulfide. Its sensitivity to mechanical influences, brisance, rate of deton, and other expl characteristics were detd at PicArs in 1940. In view of the fact that it is specially sensitive to rifle bullet impact, and has a rate of deton and brisance considerably lower than TNT, it was concluded that Myrite is not suitable for use as a military expl

Ref: C.J. Bain, "Investigation of the Explosive 'Myrite'", PATR 1030 (1940)

Myrobalan. The dried fruits of certain Indian and Chinese trees, contg about 30% tannin. After extrg the tannin, the powd material was used as an ingredient of some commercial expls.

Refs: 1) Hackh's (1944), 555-L 2) Cond-ChemDict (1950), 455

Myrobalan Explosive. Commercial blasting expl contg myrobalan 36, K nitrate 28 & Amm perchlorate 36%

Ref: D. Kilburn, FrP 389905 (1908) & CA 4, 2733 (1910)

Myrol. A Ger liq expl consisting of a soln of methyl nitrate in methanol or other solvents. The term Myrol was also used to designate straight methyl nitrate. The material prepd prior to WWII, by cautiously adding methanol to a mixt of nitric and sulfuric acids, proved to be impure, unstable in storage and very sensitive to heat and shock. During WWII, Walter et al (Ref 2), developed a continuous method of manuf of methyl nitrate from methanol and dil nitric acid, which gave a pure and much more stable product than that prepd previously. A detailed description of the method of prepn is given in Ref 2, pp 9—10. Pure methyl nitrate proved to be an expl more powerful than NG, with a brisance exceeding any other HE known, and with a sensitivity to shock comparable to that of PETN. Pure methyl nitrate is a clear mobile liq with a bp of about 63°, and is insol in w.

Inasmuch as methyl nitrate is very sensitive to mechanical action, it was found much safer to use it in methanol soln. Such solns, called Myrol, may be obtained directly in the methyl nitrate manufg process, since all that is necessary is to use an excess of methanol. One of the most suitable solns proved to be an azetroptic mixt consisting of about 75% methyl nitrate and 25% methanol. This mixt has a bp of 57.5°.

Myroals contg at least 25% methanol will not evaporate to leave 100% methyl nitrate

Römer (Ref 1) calls Myrol a mixt contg 73% methyl nitrate and 27% technical methanol contg 4% w. Tschinkel (Ref 3) states that Myrol consisted of 80 wt % methyl nitrate and 20 wt % methanol.

Following are some props of methyl nitrate—methanol mixts: vel of deton ranging from 2400—4900 to 7500—8200 m/sec, gas vol about 873 l/kg, Qe 1640—1700 kcal/kg, power and brisance — comparable to those of NG, sensitivity to shock — comparable to that of DNB, and toxicity — comparable to that of aliphatic
nitrates, such as NG and PETN. Like NG, Myrol causes headaches and pulse excitation, but they disappear more rapidly than with NG. Caffein or coffee proved most successful in decreasing pulse excitation.


Myrol Explosives. Methyl nitrate (qv) and its mixts with methanol, benz, NB, etc found extensive application by Ger in WWII as ingredients of numerous liq, plastic and solid prop farms and expls. Some of these mixts were known as Ersatzsprengstoffe (substitute expls). In the case of liq expls and proplnts, Myrol (methyl nitrate plus methanol) was used either by itself or in mixts with liqs such as benz, MNB, etc. For use as a plastic expl or proplnt, Myrol was treated with small quantities of NC to form a soft jelly. As a solid expl or proplnt, it was treated with 25–30% NC to form a hard jelly, or was mixed with the usual sol ingredients of dynamites, such as kieselguhr, sawdust, inorganic nitrates, lignin, etc. Because of the fact that Myrol is a volatile liq, all mixts contg it had to be kept in air-tight containers.

Several Myrol manufg plants were constructed in Ger during the latter part of WWII, and total capacity was as great as 20000 metric tons per month. The largest of these plants was the Christianstadt Fabrik of Dynamit A-G, with a capacity of 400 tons per month.

Myrol expls were used for the following purposes: (1) Liq Myrol mixts were used as rocket proplnts, as charges for bangalore torpedoes, land mines, bombs, special fuzez, and for clearing trenches, foxholes, etc; (2) Plastic Myrol mixts were used as military demolition charges and mining expls; (3) Solid Myrol expls were used as bursting charges in land mines, the 50-kp projector mine, hand grenades, V-1 and V-2 rocket warheads, the bursting charge of Panzerfaust (anti-tank shaped charge), boosters, etc.

More detailed information on Myrol ExpIs and their uses can be found in the refs:

"N" (Explosifs de Mine). Several types of older Fr mining expls: No 1a (couché), AN 95.5 & TNN 4.5%; No 1b (roche), AN 91.5 & TNN 8.5%; No 1c, AN 87.4 & DNN 12.6%; No 1d, AN 82.4, DNN 12.6 & Ba nitrate 5%; No 2, AN 80 & MNN 20%.
Ref: Daniel (1902), 448

**N**<sup>15</sup>, Reactions with. The course of the reaction between diazomethane and hydrazoic acid was studied using N<sup>15</sup>-labeled reactants. It was also found that labeled methyl azide could be reliably analyzed by decomp with HI, and that unambiguously N<sup>15</sup>-labeled methyl azide could be made by treating methylurea with HN<sup>15</sup>O<sub>2</sub> and decomposing the product with KOH to CH<sub>2</sub>N<sub>2</sub>N<sup>15</sup> (Ref 2). Another study noted that in the course of the diazotization of benzhydrazide and 2,4-dinitrophenylhydrazine with HN<sup>15</sup>O<sub>2</sub>, only azides of the structure R-N=N=N<sup>15</sup> were formed (Ref 1).

**N57.** An older Italian proplnt used in 57mm guns. Its compn is similar to that of the American Maxim-Nordenfeldt powder (see in this Vol, p M46-R
Ref: Daniel (1902), 448

**NACO (Navy Cool).** A type of proplnt developed by the US Naval Ordnance Station, Indian Head, Md. It burns at temps 300° cooler than standard propulnts, thereby reducing gun-barrel wear by more than 50 percent (Ref 3). A typical formulation contains NC (12.00% N) 87.30, K sulfate 3.30, basic Pb carbonate 1.19, butyl stearate 4.16, ethyl centralite 1.03 & total volatiles 3.02% (Refs 1 & 2).

**Nahsen Dynamites.** Contained creosote to lower the freezing point of the mixt. A typical formulation contained creosote 41.5, NG 25.0, K nitrate 18.0, rye flour 9.0, collodion cotton 1.0 & Na bicarbonate 5.5%
Ref: Daniel (1902), 449

**Nahsen Explosives.** Several commercial expls of the carbonite type were patented in 1899 by Sprengstoffwerke Dr R. Nahsen & Co of Hamburg, Ger. One was named “Phoenix Powder” and contained NG 29.5, K nitrate 32.0, wood meal 38.0 & collodion cotton 0.5%

**Nail Test.** A simple, inexpensive test for comparing the performance of detonators, developed at the Explosives Experimental Station of the US bureau of Mines by C. Hall (Refs 1 & 2). The test depends on the angle formed by a standard iron nail when a detonator is fired in close proximity to it, and gives a rough indication of the side blow of the detonator. Tests of this type should be used only for comparing constancy of manufacture in a single type of detonator. Its use in comparing detonators of different constructions can be grossly misleading.

**Nansenit.** A Russian pre-WW1 mining expl containing AN 68, K nitrate 4, DNT 7, Na chloride 15 & vegetable oil 6%
Ref: Anon, SS 12, 409 (1917)

**Naoûm, Phokion (1875–1951).** German scientist specializing in expls. He was associated for over 40 years with Dynamit A-G vorm Alfred
Nobel & Co, at Schlebusch-Manfort, and published works on NG, Nitrosugar, Dinitroglycol, coal mine expls, etc. He was also the author of books dealing with expls, such as: "Scheiss-und Sprengstoffe", T. Steinkopf, Dresden & Leipsig (1927) and "Nitroglycerin und Nitroglycerin-sprengstoffe", J. Springer, Berlin (1924). The latter work was translated into English by E.M. Symmes ("Nitroglycerin and Nitroglycerin Explosives") and published by Williams & Wilkins Co, Baltimore, Md, in 1928

Ref: A. Berthmann, AngChem 63, 249–50 (1951)

Napalm (Thickened Fuel). An acronym for N Aphthenic acid and PAL Metate, the former being a petroleum product, while the latter is extracted from palm oils. Napalm was developed by Dr Louis F. Fieser of Harvard University and a group of colleagues in 1941–42 under the sponsorship of the National Defense Research Committee. Although a patent was filed in 1943, because of national security implications, issuance of the patent was delayed until 1952 (Ref 3). Dr Fieser and his group began the search for a gasoline thickening agent for use as a flamethrower fuel shortly before Pearl Harbor. Their early work concerned the possible use of rubber mixed with gasoline, however, with rubber supplies cut off by the Japanese, the scientists had to seek some other means. Their research led to Napalm which consisted basically of the Al soaps of coconut fatty acids, Al naphthenate, and unsaturated fatty acids (Ref 4). The term Napalm has, over the years, been used to denote the total thickened fuel

Napalm has been used as an incendiary filler for air-to-ground bombing as well as a fuel for flamethrowers. The jellied composition, the extremely high temp produced on ignition, and its low cost make Napalm an ideal weapon against "soft" targets such as humans and most kinds of primitive dwellings. It is also extremely effective against armored vehicles, because their armor operates as a heat conductor which boils the crew inside. Since it flows as a liq it can also be used against concrete bunkers and similar fortifications, although most modern fortifications have over-hanging lips above the firing slits intended to prevent the fluid from flowing inside. Napalm is not suitable for use against "hard" structures such as bridges. An operational problem with Napalm is that its density is low so that tanks filled with it are bulky in relation to their weight, and this reduces the speed of carrying aircraft. The intense heat produced by Napalm can "kill" armored vehicles even if only a near-miss is scored, so that it is far superior to an explosive bomb for this mission (Ref 8)

Langstroth and Hart (Ref 1) detd the heat capacities of gasoline, Napalm, and various Napalm-gasoline gels by the method of mixts using an adiabatic calorimeter in the range of $-50^\circ$ to $50^\circ$. The specific heat in cal per g per degree at temp $T^\circ$ within this range is given by: $S_T = 0.479 - 0.00054C + 0.00092T$ where C denotes the Napalm concn by wt

There are presently three common fuel thickeners used by the US Armed Forces. These are M4 thickener (Standard A); M1 thickener (Standard B); and M2 thickener (Air Force Standard A)

M4 Thickener: It is a fine, white powder which is a by-product of petroleum. Chemically, it is a diacid Al soap of isooctanoic acid. As a general comparison with M1 thickener (the original Napalm), only one-half as much M4 thickener is needed to obtain thickened fuel of the same consistency, an unpepetized gel can be obtained at lower temps, and the aging time is shorter. It is much less susceptible to moisture in the air, and has a higher density than the other thickeners, which gives it a decided logistic advantage. Fuels prepd with M4 thickener are superior in flamethrower firing performance with respect to range, burning, and target effects as compared with fuels prepd with other available thickeners (Ref 6, p 41; Ref 7, p 8)

M1 Thickener: It is a coarse, granular material ranging in color from light tan to brown. Chemically, it is a coprecipitated Al soap of naphthenic, oleic and palmitic acids in the approx ratio of 1:1:2. The three main disadvantages accruing from the properties of M1 thickener are (1) it is a critical wartime material since it is made from coconuts; (2) it is extremely hygroscopic, and the presence of water decreases its ability to form a stable thickened fuel. In addition, the relatively large
particles of the thickener permit circulation of air into the bulk of the material, causing extensive absorption of moisture. Thus, a partially used container of M1 thickener should be discarded; (3) M1 thickener is too coarse to be used in continuous flow mixers, and can only be used for hand mixing or small field mixing unit operations (Ref 7, p 8)

When M1 thickener is stirred into gasoline at a temp ranging from 16° to 29°, it swells until the entire volume of gasoline becomes a more or less homogeneous gel. The gel may vary in consistency from a pourable fluid to a rubbery material, depending upon the proportion of thickener added. This type of gel, if allowed to set undisturbed, assumes a semirigid jelly-like form. If the gel is shaken violently, stirred vigorously, or squirted thru a small opening under pressure, it becomes almost liq again, but resumes a jellylike form upon standing. The percentage of M1 thickener used ranges from 2 to 12% (Ref 6, p 41)

M2 Thickener: It is pulverized M1 thickener with an antimoisture substance (attasorb clay) added in the ratio of 1p attasorb clay to 19p M1 thickener. It readily absorbs moisture from the air, but not to the extent of M1 thickener, because less air circulates thru the pulverized particles; the attasorb clay further lowers moisture absorption. A container may be resealed after part of the M2 thickener has been used provided it has had minimum exposure to air. Since M2 thickener is composed mainly of M1 thickener, it retains most of the characteristics of M1, including the disadvantages of being manufd from critical material, absorption of water from the air, and sensitivity to moisture. As a general comparison with M1 thickener, only two-thirds as much M2 thickener is needed to obtain thickened fuel of the same consistency (Ref 7, p 9)

Peptizers are used to hasten the gelling of gasoline and thickener in cold weather. They are used, however, only when very low temps make mixing time excessively long and heating the gasoline is not possible, since they cause the mixt to break down after a short period of time (less than 48 hrs). Cresylic acid is used when preparing thickener fuel using M1 or M2 thickener and gasoline at temps below 60° F. When preparing thickened fuel using M4 thickener and gasoline at temps below 40° F, 2-ethylhexanoic acid is used. Unpeptized gels can be obtained with M4 thickener when gasoline temps are as low as 0° F, but mixing time is very long (Ref 7, p 9)

In most cases, incendiary munitions containing thickened fuel are equipped with white P igniters to insure ignition because the bursting charge may or may not cause ignition. Since ignition of white P is prevented by water, a Na igniter is used in munitions to be dropped over water. Thickened fuel in portable flamethrowers is ignited by a red P-tipped metal match which scratches an igniting mixt (Ref 6, p 42)

See also under Flame Throwers — Liquids and Gels in Vol 6, F57-L ff

Written by S. M. KAYE


Naphthas. Flammable liquids, consisting mainly of hydrocarbons of the C₅H₁₀+ series, obtained by distillation of petroleum, oil shale, coal tar or wood, bp range 95 to 220°. The principle varieties of naphthas are (a) Light or Cleaner’s Naphtha: white, vol petroleum distillate used as a cleaning fluid, bp range 95 to 150°; (b) Heavy Naphtha: dark amber to dark red liq consisting of xylene and higher homologs, d 0.885–0.970 g/cc, bp range 160 to 220°, flash p 100° F. Has been used in Sprengel type expls as a fuel
Ref: 1) CondChemDict (1971), 602 2) Hackth’s (1972), 444

Naphthas, Hydroformed. Produced by the Standard Oil Development Co (Ref 1) by passing
vapors of certain petroleum fractions together with H₂ over a catalyst composed of the oxides and/or sulfides of metals of group VI of the periodic table, in the presence of promoters. The reaction takes place above 20 atm press and above 452°F, with suitable H₂ partial press and contact time necessary to obtain destructive hydrogenation without the formation of polymerized material. The resulting hydroformed naphthas may be halogenated, sulfonated or nitrated.

**Nitrated Hydroformed Naphthas.** The nitration of hydroformed naphthas with mixed nitric-sulfuric acid cong a small amt of w (Ref 2) produced materials which may be used either in expls or as intermediates in the dye industry. It is also possible to reduce the nitrocompounds to amines which can be used as flash reducing agents in proplnts. Refs: 1) Standard Oil Development Co, BritP 477515 (1937) & CA 32, 3951 (1938)
2) Standard Oil Development Co, BritP 477014 (1937) & CA 32, 3964 (1938)

**Solvent Naphtha (160° benzol).** A mixt of small percentages of benzene and toluene with xylene and higher homologs from coal tar. In crude form, a dark straw-colored liq, bp about 160° (80%), d 0.862–0.892g/cc, flash p about 78°F. When refined, a w-white liq, bp about 160° (90%), d 0.862–0.872g/cc, flash p about 78°F. May be obtained from coal tar by fractional distillation. When nitrated, used in Dynamites (Ref 5)

**Nitrated Solvent Naphtha (N.S.N.).** As nitration of crude solvent naphtha by the usual one-stage method results in yields that are too low, because of oxidation, E. Blecher et al (Ref 3) proposed nitrating only the refined material, and in two stages. The two-stage method is described in Colver, pp 255 & 686–87 (Ref 4). The product consists chiefly of 2,4,6-Trinitromesitylene (see under Mesitylene and Derivatives in this Vol), and 3,5,6-trinitropseudocumene, with small quantities of the nitrated products of xylene, ethylbenzene, etc.

N.S.N. may be either solid or liq (oil); both forms are highly expl and have been used in commercial, and to a certain extent, in military expls. Typical examples follow: (1) Explosive patented by Schultz & Gehr (Ref 1):

AN 76, N.S.N. 10, K nitrate 10, K perchlorate 2 & resin 2%; (2) Explosives patented by Distler, Blecher and Lopez (Refs 2 & 3): (a) AN 88 & N.S.N. 12%; It is insensitive to shock or percussion and does not explode when heated to 200° or when ignited in an open flame, but detonates with considerable brisance when strongly initiated. The brisance may be reduced by substituting either K nitrate or Amm perchlorate for part of the AN. (b) AN 85, N.S.N. 12 & Pb or Ba dioxides 3%. This mix is more brisant than (a). (c) AN 85, N.S.N. 12, Pb or Ba dioxides 1% & finely pulverized Cu 2%; an extremely brisant expl. (d) Brisant expls were prep'd by mixing solid or liq N.S.N. with PA in all proportions. (e) Gelatinous dough-like expls can be prep'd by dissolving 60% of collodion cotton in 94p of oily N.S.N., preheated to 100°. (f) By incorporating, with warming, 30–40% of AN plus flour into the above mixt (e), a solid mass is obtained which may be pulverized and used in lieu of Dynamites. Refs: 1) G. Schultz & F. Gehr, USP 894707 (1906) 2) C. Distler, E. Blecher & C. Lopez, FRP 380996 (1907) 3) E. Blecher, C. Lopez & C. Distler, USP 898144 (1908) 4) Colver (1918), 255 & 686–88 5) CondChemDict (1971), 603

**NAPHTHALENE AND DERIVATIVES**

*Naphthalene* (Tar Camphor), Naphthalin (Ger), Naphthalene (Fr), Naftalene (Sp), Naftalina (It), Naftal (Russ); C₁₀H₈, mw 128.16, mp 80.2°, bp 217.98°; d₄ at 100° 0.9628g/cc, RI at 100° 1.5821 (Ref 4), Qₚ 5151.23kJ/mole, Qₚ 18.57 ± 25kcal/mol (Ref 10); CA Registry No 92-24-0. Colorless, volatile flakes from EtOH with a strong coal-tar odor; may be obtained from coal gas, from the fraction of coal tar boiling betw 170 and 230°, or from petroleum. The naphthenic fraction is aromatized, fractionated to give an alkyl-naphthalene cut, and the latter dealkylated to naphthalene. In 1965, ca 3/8 of the naphthalene produced in the USA was made this way, the remainder being obtained from coal tar (Ref 11); 321 isolations and prepns of naphthalene are reported in Ref 5. It is sl sol in w (0.003g/100ml at 25°); sol in EtOH (91.5g/100ml at 19.5°); and very sol in hot EtOH, eth, C tetra-chloride, C disulfide, and bz (Refs 1 & 13). It is
purified by repeated sublims followed by recryst from EtOH or bz. A procedure for the accurate detn of purity by a differential heat loss ap is described in Ref 6. It can be identified as the picrate, mp 149° (Ref 9); or the 2,4,7-trinitrofluorenone complex, mp 151.2—4.0° (Ref 3). It can be detd in petroleum prods by IR (Ref 8), and quafy in mixts with tetralin and decalin by gas chromatography (Ref 7). It is toxic in “large doses” (Ref 12) and has a rating of 2 in Sax for skin contact and inhalation toxicity. The flammability is moderate, and it reacts with strong oxidizers (Ref 14). Its ign temp in air and O2 are 587° and 560° resp; the temp limits of infl of air sad with naphthalene vapor at 746—8mm are 77.8° and 121.8° resp; and the flamy limits in air are 0.88 and 5.9% by vol (Ref 2)

Uses. Naphthalene and its derivatives find uses as starting materials for the prep of dyestuffs, pharmaceuticals, pest control agents, and expts (Ref 11). It is one ingredient in the exp “Dalmenite A” (see Vol 3, D1-R)


Azidonaphthalenes, Naphthyl Azides

Monoazidonaphthalenes, C10H7N3, mw 169.18, N 24.84%

1-Azidonaphthalene (Alpha-naphthyl azide). A pale yel oil which solidifies at 12° to lustrous yellow prisms, decomp at 110° with N evolution (Refs 1 & 3), d at 24.9° 1.1731g/cc (Ref 4); it can be steam distd (Ref 2); CA Registry No 6921-40-4. It is prepd by the action of hydrazoic acid (Ref 3), or hydroxylamine sulfate (Ref 4) on 1-naphthalenediazonium salts. It decomp in boiling Ac2O to give 20% 2-amino-1-naphthol and 28.5% 2-naphthylamine (Ref 6). When frozen on a cold surface at liq N temp and photolyzed with a Hg arc lamp, it forms 1-naphthyl nitrene (R-N:) which dimerizes to 1,1’-azanaphthalene upon warming (Ref 7). The photosensitized decomp is studied in Ref 8, with kinetic and mechanism data given

1,2-Azidonaphthalene. Crysts from petr eth (bp 60—90°), mp 108°; prepd in four steps starting with 1-nitro-2-naphthylamine (Ref 3). It decomp in boiling decalin to evolve N and form

\[ \text{HC} \quad \text{CN} \]

The mechanism of this reaction is discussed in Ref 3

1,8-Azidonaphthalene. Pale yel crystals, mp 95—100° with decomp; prepd by the bis-diazotation of 1,8-diaminonaphthalene followed by treatment with Na azide (Ref 5). It has been patented as a photosens intermediate in a photocopying process (Ref 6)

2,3-Azidonaphthalene. Needles from petr eth (bp 40—60°), mp 63—4°; prepd in five steps starting with 3-amino-2-naphthoic acid. Its pyrolysis in a Pyrex tube at 400° gave
2,7-Diazidonaphthalene. Almost colorless leaflets from petr eth, mp 98°, turns red on exposure to light; prepd by the action of Na azide on 2,7-naphthalenedicarboxylic acid sulfate (Refs 1 & 2). It has been patented as a cross-linking agent for polyethylene and polybutadiene (Ref 4).


Azidonitronaphthalenes

Monoazidononitronaphthalenes, \( C_{10}H_{10}N_4O_2 \), mw 214.18, N 26.16%, OB to CO \( \text{O} \) -153%. Eight isomers are present in the literature.

1-Azido-2-nitronaphthalene (2-Nitro-1-naphthyl azide). Long yel needles from aq acet, mp 103-4° with decompn (Refs 1 & 4); CA Registry No 16714-21-9. Prepd by the action of Na azide on 2-nitro-1-naphthalenediazonium sulfate with urea in glacial acet ac (Ref 4). It decomposes at 150° with N evolution, and in toluene at 110° to give a 90% yield of

![Structure](image)

(Ref 5)

1-Azido-4-nitronaphthalene (4-Nitro-1-naphthyl azide). Yel needles from hot EtOH, mp 99°; CA Registry No 6549-18-4. Its prepn is the same as above, using the 4-nitrodiazonium salt (Refs 1 & 4).

1-Azido-5-nitronaphthalene (5-Nitro-1-naphthyl azide). Yel needles from hot abs EtOH, mp 121°; prepn the same as above using the 5-nitrodiazonium salt; decomps rapidly at 130° with N evolution (Refs 2 & 4).

1-Azido-8-nitronaphthalene (8-Nitro-1-naphthyl azide). Yel prisms from hot acet, mp 130-138° with decompn, darkens on exposure to light; prepn the same as above using the 8-nitrodiazonium salt (Refs 1 & 4).

2-Azido-1-nitronaphthalene (1-Nitro-2-naphthyl azide). Yel needles from acet, mp 116-17° with vigorous decompn; CA Registry No 16714-28-6. Prepd by the nitration of 2-naphthyl azide with nitric acid (v 1.42g/cc), or by the action of hydrazoic acid on 1-nitro-2-naphthalenediazonium sulfate (Refs 3 & 4). It gives the same product on pyrolysis in toluene as 1-azido-2-nitronaphthalene (Ref 5).

2-Azido-3-nitronaphthalene (3-Nitro-2-naphthyl azide). Cream needles, mp 101° with decompn; prepn same as above with the 3-nitro-2-diazoium salt. It decomps on heating to give tars, but no furoxan (Ref 6).

2-Azido-5-nitronaphthalene (5-Nitro-2-naphthyl azide). Brown yel needles from acet, mp 133.5°; prepn same as above with the 5-nitro-2-diazoium salt; stable in hot eth acet and hot glacial acet ac (Ref 4).

2-Azido-8-nitronaphthalene (8-Nitro-2-naphthyl azide). Yel prisms from aq acet, mp 108°; prepn same as above from the 8-nitro-2-diazoium salt (Refs 3 & 4).


1-Azido-2,4-dinitronaphthalene (2,4-Dinitro-1-naphthyl azide). \( C_{10}H_{12}N_2O_4 \), mw 259.18, N 27.02%, OB to CO \( \text{O} \) -114%; yel needles, mp 105° with decompn; prepd by the action of Na azide in boiling abs EtOH on 1-chloro-2,4-dinitronaphthalene, yield 75%.


Azo Derivatives of Naphthalene

1-Bromo-1-nitro-1-(2-naphthylazo)ethane.

![Structure](image)

mw 308.14, N 13.64%, golden yel leaflets from EtOH, mp 168° with decompn; prepd by the action of Br on

in warm EtOH (Refs 3 & 5)
1-(2-Naphthylazo)-1-nitro-1-nitrosoethane.

\[
\begin{align*}
\text{NO}_2 & \\
\text{N:NCCH}_3 & \\
\text{NO} & \\
\text{N:NCCH}_3 & \\
\text{NO} & \\
\text{N:NCCH}_3 & \\
\text{NO} & \\
\text{N:NCCH}_3 & \\
\text{NO} & \\
\text{N:NCCH}_3 & \\
\text{NO} & \\
\text{N:NCCH}_3 & \\
\text{NO} & \\
\end{align*}
\]

mw 258.23, N 21.70%, OB to CO₂ -161%; dark-red needles from EtOH, mp 141° with decomp; prep'd by the action of Na nitrite and aq HCl on the same raw material as used above (Refs 3 & 5)

2,4,6-Trinitrophenylazonaphthalene-1, picrylazo-1-naphthalene. C₁₆H₆N₅O₆, mw 367.27, N 19.07%, OB to CO₂ -133%; red-yel needles, mp 226° with decomp;

prep'd by the oxidn of the hydrazine with chromic acid in glas acet ac (Refs 1 & 4)

2,4,6-Trinitrophenylazonaphthalene-2 (Picrylazo-2-naphthalene). Dull red needles from glas acet ac, mp 205° with decomp (Refs 3 & 4)


Nitro Derivatives of Naphthalene

Mononitronaphthalenes (MNN), C₁₀H₇NO₂, mw 173.16, N 8.09%, OB to CO₂ -198%

1-Nitronaphthalene (Alpha-nitronaphthalene, 1-MNN). Yel needles from EtOH, mp 61.5° (Refs 1 & 6), bp 304° (Ref 4); CA Registry No 86-57-7

1-MNN is readily prep'd from naphthalene by the action of a number of nitrating agents. Some which have been used are concd nitric ac in the cold for 5-6 days (Ref 3); N dioxide in the cold (byprods are also obtained) (Ref 5); nitrilsulfuric ac (O₂NSO₃H) in 100% nitric ac at 30°, yield quant (Ref 13); concd nitric ac and anhyd Zn chloride in pyridine at 130° (Ref 11); a suspension of Na nitrite in concd sulfuric ac at 110° (Ref 14); di-N tetroxide in concd sulfuric ac, yield 88.4% (Ref 15); and in low yield by heating with Bi trinitrate (Ref 12). On a coml scale the nitrination is conveniently done with mixed acids such as 83g of nitric (d 1.38 g/cc) and 233g of sulfuric (d 1.83g/cc/100g of naphthalene, yield 85% (Ref 19). Lab and coml prepns are summarized in Ref 22, p 350. In Ref 8 are discussed the effects of acid concns on the formn of mono- and polynitro compds by the mixed acid nitratn of naphthalene. Other studies on the coml prodn of 1-MNN are in Refs 16, 20, 29 & 30

Analysis. 1-MNN is best identified by redn to the amine with Sn and 10% HCl, which is converted to the benzenesulfonamide, mp 167°, or the benzamide, mp 160° (Ref 36). The picrate, CA Registry No 29754-26-5, is also known (Ref 37). It has been found in crd TNT recovered from Comp B (probably an. ng from the presence of naphthalene in coml toluene), from which it was isolated by gas chromatography and identified by mass spec (Ref 40). Standard anal procedures for Mil grade 1-MNN are given in Ref 35

Flash Point. Closed Cup, 327°F (Ref 42)

Heat of Combustion. 1190.1kcal/mole at 15° (Ref 18)

Heat of Formation. Q_f^\text{HCl} = -85cal/g, Q_f^\text{HCl} = -68cal/g (Ref 27)

Mixtures. Frolova studied the system 1-MNN/TNT and found eutectics at 28.5 and 78.5% MNN, mp 58.8 and 45.5° respectively; and a dystectic point, mp 63.4°. He also found that the vsc of liq TNT is decreased by the addn of MNN (Ref 23). A mp diagram with PA shows a 1:1 molar eutectic, mp 67° (Ref 21)

UV Spectrum. In EtOH there is a peak at 3650, in petr eth at 3700, and in benz at 3450Å (Ref 9)

Uses. While 1-MNN is not an expl and cannot be detod, mixts with expls have been used extensively. A mixt of PETN/1-MNN 95/5 is used as a detonator for mixts contg TNN (Ref 24). It has been found that addn of 0.2 to 0.4% 1-MNN to TNT and 0.4 to 0.6% to Comp B will inhibit crack formn in castings of these expls (Refs 31 & 35). A mixt with TeNMe contg 80.3% TeNMe has expl props: mp 58.8°, OB to CO₂ +0.34%, d 1.57g/cc, deton vel 8160 m/sec, power by Trauzl test 489, brisance by
Hess test (Ref 17) 65.95 mm (Ref 33). A mixt with PA, called Trimonite or MMn (Fr) has the following props: comp 88–90% PA/10–12% 1-MNN, OB to CO$_2$ -62%, mp 90°, impact sensy BM app 60 cm, PA app 10°; rifle bullet impact test unaffected; expln temp, decomp in 5 sec at 315°; vacuum stab test, 9.9 cc of gas evolved in 40 hours at 120°; 200 g bomb sand test, 44.2 g of sand crushed; deton vel 7020 m/sec at a diameter of 1.0" & d of 1.60 g/cc. Prepd by melting PA and 1-MNN together in the correct proportions in a steam-jacketed kettle, with care being taken to avoid the forma of expl metal picrates. Used as a substitute for TNT in cast-loaded munitions (Refs 31 & 32). A comp of 61.7% AN, 8.0% of an equimolar mixt of 1-MNN and DNT, 0.8% guncotton, and 1.5% wood flour is an expl which can be safely mixed (Ref 28). AN is coated with 2–5% 1-MNN, 2–20% TNT is added, and the mix agitated in a rotating drum as another 2–5% of TNT is added to give a w insoluble granular expl; deton vel 6000–7000 m/sec, Trauzl test 525 cc; gap test, above 6 cm; suitable for borehole blasting (Ref 37). 1-MNN has been used in Ammonite expls (Vol 1, A307). At a level of 1.5%, 1-MNN prolongs the stab of NC from 7.5 to 25.5 hours as shown by the litmus test (Ref 25). The thermal decompn of dil solns of NC in 1-MNN was studied betw 165 and 200° by following the evolution of gas. It was found that 3.5 moles of gas were evolved for each glucoside unit present in NC (Ref 25).

2-Nitronaphthalene (Beta-Nitronaphthalene, 2-MNN). Long yel needles from EtOH & eth., mp 79° (Refs 2 & 7), bp at 14 mm 180–4°. (Ref 10); CA Registry No 581-89-5

2-MNN is obtained in 3–5% yield by the nitration of naphthalene and is present at this level in coml MNN. It is best prepd by indirect methods; for example, by the removal of an amino group from an appropriately substituted nitronaphthylamine. The amine is treated with Na nitrite and acid to form the diazonium salt which is replaced with a H atom by redn with EtOH (Ref 7). It may also be prepd by treatment of 6-nitro-1,2,3,4-tetrahydroxynaphthalene with Br to form a dibromo cmpn (probably the 1,4-isomer), followed by removal of two moles of H bromide by dist in the presence of base (Ref 10). 2-Naphthalenediazonium fluoroborate is decomp at room temp in the presence of Cu(I) chloride and Na nitrite to give 2-MNN (Ref 38). The UV spectrum in EtOH shows peaks at 3000, 3675 & 4250 Å; and in petr eth at 3200, 3750 & ca 4300 Å (Ref 9). A more recent prepn of 2-MNN is as follows: naphthale- 

lane is treated with 2 moles of hexachlorocyclopentadiene to give a 1,2:3,4-diadduct (DHA), mp 214–15° (Ref 26). Upon treatment with anhyd nitric ac in sulfonyl chloride or methyl- 

ene chloride, a mixt of 13% 1-nitro and 87% 2-nitro-DHA is obtained which can be sepd by recrystn from aq acet. Upon heating to 250–400°, the 2-nitro-DHA is converted to 2-MNN in good yield (Ref 41). The pircate of 2-MNN (CA Registry No 29754-27-6) is described in Ref 39. Because it is difficult to produce, 2-MNN has had no coml or expl uses. It has been used to prep other nitrated naphthalenes:

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Dinitronaphthalenes (DNN). C₁₀H₈N₂O₄, mw
218.16, N 12.84%, OB to CO₂ -139%

Below is collected info on mixts of DNN and
on compds of unspecified structure. The nitration
of naphthalene with mixed acid gives a 2:1 mixt of 1,8-
and 1,5-DNN contg a small amt of the 1,3-
isomer (Ref 54). This is the comp of the crtl DNN used in the expls
industry

Crude DNN can be detoned when confined
and heated, its explosibility is lower than
DNB or AN; its fire point is ca 350° (Ref 53).
It also can be detoned by an initiator when
loosely packed in shells (Ref 57)

Preparation. On a cmol scale the nitration of
naphthalene is carried out in two steps using a
cylindrical jacketed reactor 1.6 x 1m with a
conical bottom. It is fitted with a discharge
pipe 8cm in diameter and a stirrer which can be
rotated at 85-90rpm. The jacket can be heated
with steam or cooled with cold w. The cover is
provided with an opening for the addn of nap-
thalene and a vent for the removal of gaseous
prods

Procedure. a) The reactor is charged with
1150kg of mixed acid contg slightly more than
128kg of K nitrate. The comp should be nitric
ac 12-14%, sulfuric ac 40-50%, and the rema-
inder w. b) The mixt is agitated as 300kg of
naphthalene is added in small portions over a
3 hour period as the temp is allowed to rise to
50°. When all the naphthalene is added, the
reactor is heated to 55°, which melts the crude
MNN. c) The stirrer is stopped, the mixt al-
lowed to sep, and the mono-spent acid (which
is depleted of K nitrate) is drained to a holding
tank; the oily prod is transferred to a tank contg
w at 70°, and fitted with a steam jet agitator.
d) The prod is agitated for 30min with w and
steam, allowed to sep, and the oil poured into
trays where it solidifies, yield almost quant. In
Ref 27 there is a slightly different proc: e) The
MNN is broken into fist-sized pieces and added
to the nitrator contg 1150kg of a mixt of 51%
sulfuric ac, 26.5% K nitrate, and the rema-
inder w, while being agitated at 85-90rpm. f) The
temp is kept at 38-45° during the addn after
which it is raised over a one hour period to 55°.
g) The nitration is complete when the emulsion
is replaced by uniform grains of DNN. h) The
slurry is filtered thru a Nutsch filter and the
filtrate recycled to step a. i) The crude DNN is
washed with spent acid from step c, then with 6
portions of cold w. j) The DNN is transferred
to a tank with a false bottom and agitated with
6 portions of cold w at 60°. k) The DNN is
dried at 60° for 24hours, yield almost quant, w
content ca 0.5% (Ref 24). The prod is 35-
40% 1,5-, 60-5% 1,8- and 1-2% 1,3-DNN. It
is an expl, but is less powerful than DNT
Toxicity. Workers wrapping or otherwise hand-
ling TNT/DNN mixts were found to have derma-
titis as well as symptoms of systemic poisoning
(Ref 47)

Uses. Mixts of DNN with expls have been used
as substitutes for TNT by many countries when the latter was in short supply. A mix of 87.5% AN and 12.5% DNN (OB to CO\textsubscript{2} +12.5%), called Schneidery (Fr), Sznejdery (Poland), and Shnaiderit (USSR), was used in WWI as a fill for HE artillery shells (Ref 61). Another comp of 78% AN and 22% DNN was used in Fr and the USSR (Ref 61). A comp contg 80% PA and 20% DNN, called MDN or MDn (Mélenit-Dinitrophenylamine) (Fr), melts near 105°, and was used as a cast filler for projs and bombs (Ref 60). Another series of comps of AN and DNN, called Type N, Nos 1b, 1c, 1d, & 7 (Fr) are described in Ref 39. A mix of 40% TNT, 30% HNDPPhA, 20% DNN, and 10% powd Al (code name KMA Block or Ersatz-sprengstoffe) was used in Ger during WWII as a substitute for TNT (Ref 55). A mix of 50% AN, 43% TNT, and 7% DNN, called Nougat or MST (It) was cast loaded into artillery shells (Ref 60, p 339); another comp of 72.8% AN, 17.6% TNT, and 10.5% DNN, called Siperite or MNST (It) was similarly used (Ref 60, p 347). Other Italian formulations contg DNN are reported in Ref 40. Comps of 50/50 and 80/20 PA and DNN, code name Onayaku (Jap) were used as burning charges in artillery ammo (Ref 56); DNN is one ingredient of “Chanyaku” expl (Jap) (see Vol 2, C148); and a comp contg 79% AN, 10% DNN, 10% Na chloride, and 1% sawdust, code Shon Bakuyaku (Jap) was used as a demolition expl (Ref 56, p 113). A similar comp of 51.5% PA and 48.5% DNN, code Russian Alloy (Russki Splav) (USSR) was used in WWII in artillery ammo Recent Uses: Mixts of 15–45% DNN, 15–45% Hexogen, and 5–30% powd Al are useful blasting expls (Ref 37). AN (918g) is mixed with 80g of DNN or TNT in 80g of concd nitric ac, and gaseous ammonia passed in until the mixt is neutral, to give an expl (Ref 44). A mixt of 26 parts polystyrene, 5 DNN, and 300 benz is added to 612ps of Pb dioxide, and the mixt dried to give a comp useful for match heads or fuses (Ref 51). At a level of 1.5%, DNN prolongs the life of NC by 6.5–7.5 hours at 106.5° as indicated by the litmus test (Ref 59). A comp of 87% AN, 4% DNN, 4% TNT, 2% Na stearate, and 3% starch is kneaded, pressed, and packed into cylinders (sticks), packing d 1.3g/cc, bri-sance equal to NG Dynamite (Ref 46)

1,2-Dinitrophthalene (1,2-DNN). Brownish needles from EtOH, mp 158° (Refs 5 & 20); CA Registry No 24934-47-2. It is prepd by bromination of 5,6-dinitro-1,2,3,4-tetrahydrophthalene followed by dehydrobromination (Ref 20), from 2-nitro-1-naphthaldehyde by the same procedure as used for the prepn of the 1,4-isomer (Ref 20)

1,3-Dinitrophthalene (Gamma-dinitrophthalene, 1,3-DNN). Bright yel needles from aq pyridine, mp 144°, bp subl (Refs 1 & 32); CA Registry No 605-37-1. It is prepd by the action of nitric ac/sulfuric ac on naphthalene at low temps (Refs 14 & 33); by the nitration of 1-MNN with a mixt of 17.3% nitric ac, 61.2% sulfuric ac, and 21.5% w, temp 59–75°, time 90min (Ref 52); by the action of powd Cu (Ref 18) or hydrazine (Ref 22) on 1-chloro-2,4-dinitrophthalene; by the diazotization of 2,4-dinitro-1-naphthaldehyde followed by redn of the diazonium salt with EtOH (Ref 25); or by the action of Br on 5,7-dinitro-1,2,3,4-tetrahydrophthalene followed by dehydrobromination (Ref 13). It is used to prep more highly nitratd naphthalenes

1,4-Dinitrophthalene (1,4-DNN). Long yel needles from MeOH, mp 134° (Refs 6 & 34); CA Registry No 6921-26-2. It is prepd by the diazotization of 4-nitro-1-naphthaldehyde followed by treatment of the diazonium salt with powd Cu and Na nitrite (Ref 45)

1,5-Dinitrophthalene (Alpha-dinitrophthalene, 1,5-DNN). Six sided needles from acet ac, mp 219° (Refs 2 & 29, d at 18° 1.602g/cc (Ref 48); Q\textsubscript{c} 1152.6kcal/mole (Ref 29), Q\textsubscript{f} –61cal/g (Ref 34); CA Registry No 605-71-0. It is prepd by heating naphthalene with concd nitric ac (Ref 12); by treating naphthalene with sulfuric ac/nitric ac at –60 to –50° (Ref 14); or by the nitration of 1-MNN with a mixt of 1 part of nitric ac (d 1.4g/cc) to 2ps of concd sulfuric ac (Ref 16). It forms a solid ppt with Nitron (for structure of Nitron see Ref 50), mp 202° with decompn, which can be used for identification (Ref 41). Crystals of 1,5-DNN are monoclinic tablets whose crystallographic data, including n, interfacial angles, and X-ray diffraction data are given in Ref 42. A procedure is described in Ref 43 for the analysis of expls contg 1,5-DNN by solv extrn. It is best extd with et acet
1,6-Dinitronaphthalene (Delta-dinitronaphthalene, 1,6-DN). Crystals from acet ac, mp 166–67°, bp at 10mm 235°, 360° with decomp (Refs 2 & 31); CA Registry No 607-46-5. It is prepd by the nitration of 2-nitronaphthalene with nitric ac/sulfuric ac in hot acet ac (Ref 21); by diazotization of 5-nitro-2-naphthylamine followed by treatment of the diazonium salt with Na cobaltinitrite, yield 40% (Ref 36); or by removal of the amino group from 1,6-dinitro-2-naphthylamine by diazotization followed by redn (Ref 17). The temp of expn is 492° (Ref 17)

1,7-Dinitronaphthalene (1,7-DN). Yellow crystals from EtOH, mp 156° (Refs 7 & 21); CA Registry No 24824-27-9. It is prepd by the nitration of 2-nitronaphthalene with nitric ac/sulfuric ac in hot acet ac (Ref 21); or by the diazotization of 8-nitro-2-naphthylamine, followed by treatment of the diazonium salt with Na cobaltinitrite (Ref 35)

1,8-Dinitronaphthalene (Beta-dinitronaphthalene, Peri-dinitronaphthalene, 1,8-DN). Tablets from chl or pyridine (Refs 4 & 16), mp 172.5–3.0° (Ref 29), d at 18° 1.575g/cc (Ref 48), Qf 1164.45kcal/mole (Ref 28), 1f 60cal/g (Ref 49), temp of expn 445° (Ref 19); CA Registry No 602-38-0. It is prepd by heating naphthalene with concd nitric ac (Ref 11); or by allowing naphthalene to stand in the presence of concd nitric ac for 24 hours, then warming the mixt on a w bath with concd sulfuric ac (Ref 15). It forms a eutectic with TNT contg 18.07% DNN, mp 73.4° (Ref 38). A procedure is described in Ref 43 for the analysis of exps contg 1,8-DNN by solvent extrn. It is best exctd with acet

2,3-Dinitronaphthalene (2,3-DN). Yel needles from MeOH, mp 170.5–1.0° (Refs 8 & 23); CA Registry No 1875-63-4. It is prepd by bromination of 5,6-dinitro-1,2,3,4-tetrahydro-naphthalene followed by dehydrohalogenation (Ref 23); or by nitration of a naphthalene-exchalcroliopeniadene adduct (Diels-Alder), followed by pyrolysis to regenerate the 2,3-DNN (Ref 58)

2,6-Dinitronaphthalene (2,6-DN). Long yel needles from AcO, mp 279° (Refs 9 & 30); CA Registry No 24824-26-8. It is prepd by the diazotization of 6-nitro-2-naphthylamine followed by treatment of the diazonium salt with powd Cu and Na nitrite (Ref 21), or Na cobaltinitrite (Ref 25); or from naphthalene-2,6-bis (diazonium salts) by treatment with nitrosyl-sulfuric ac (ONSO3H) in concd sulfuric ac followed by cuprocupric sulfate (Ref 30)

2,7-Dinitronaphthalene (2,7-DN). Yel crystals from AcO, mp 234°; CA Registry No 24824-27-9. It is prepd by the decarboxylation of 3,6-dinitronaphthalene-1,8-dicarboxylic ac with powd Cu in boiling quinoline (Refs 10 & 26)


5,7-Dinitronaphthalene-1-sulfonic Acid. Needles from w, mp expls around 300° when heated on a Pt foil (Refs 1 & 5). It is prepd by the action of an excess of fuming nitric ac on the sulfam: O₂S—NH

(Ref 5); or by sulfonation of 1,3-DNN with an excess of 100% sulfuric ac contg a small amlt of oleum (Ref 7)

4,5-Dinitronaphthalene-2-sulfonic Acid. Crysts, mp expls on heating (Refs 2 & 4). It is prepd by sulfonation of 1,8-DNN with 20% fuming sulfuric ac at 140° (Ref 4), or by nitration of 2-naphthalsulfonic ac with mixed ac at 0–15° (Ref 2)

4,8-Dinitronaphthalene-2-sulfonic Acid. Solid which expls on heating; prepd by nitration of 8-nitronaphthalene-2-sulfonic ac with mixed ac at 0–15° (Ref 2)


Trinitronaphthalene, C₁₀H₈N₃O₆, mw 247.16, N 15.97%, OB to CO₂ -100%

Commercial Trinitronaphthalene (TNN, Naph- tite). Yel crystal solid, mp 110–140° depending on prepn procedure used. It contains varying proportions of 1,2,5-, 1,3,5-, 1,3,8-, and 1,4,5-TNN (for descriptions of pure isomers see below)

Preparation 1) By the nitration of naphthalene: on boiling with fuming nitric ac for 14 days, TNN, mainly 1,3,8- is formed (Ref 5); by nitration with nitric ac/sulfuric ac at -60°, the same TNN is formed along with MNN and DNN (Ref 25); and with excess N dioxide at 100°, 1,3,8-TNN is formed (Ref 22). 2) By the nitration of 1-MNN: 1800kg of mixed ac (55% sulfuric ac, 40% nitric ac, and 5% w), to which is added 800kg of spent ac from a previous run, is agitated at 55° as 850kg of molten 1-MNN is added slowly. After all is in, the mixt is stirred for 2hrs at 55°, cooled to 40°, the TNN filtered from the spent ac which is recycled, and purified as is described above for DNN; yield is 120kg/100kg of MNN (Ref 19). 3) By the ni-
tration of DNN: 100kg of DNN is introduced rapidly with stirring into 400kg of mixed ac (71% sulfuric ac, 20% nitric ac, and 9% w) as the temp is held at 65° for 1 hour, then raised to 95° and held there 3 hours. The crude prod is sepd and purified as for DNN, yield 110kg (Ref 20).

TNN is an expl, more powerful than DNN, but less than DNB. Theoretical expln press is 83% of TNT (Ref 14); and its deton vel is from 6470m/sec at d 1.60g/cc to 9600m/sec at d 0.9 g/cc, both at 180° (Ref 30). It shows only incipient deflagration to deton transition at d 0.55—0.63g/cc and 1200—1600 atm (Ref 35). An expln, however, on 4 Apr 1940 in a plant at Sainte-Chamas, Fr, which was mfg TNN, caused the deaths of 11 workers (Ref 29).

Uses. Belg comp: Sabulite. 52% AN, 9% TNN, 9% K perchlorate, 4% TNT, and 26% Na chloride is a mining expl (Ref 36, p 196); Mino-
lite Antigsoloutae: 72% AN, 23% Na nitrate, 3% TNT, and 2% TNN is a currently-used permissible mining expl (Ref 12, p 194).

Fr comp: A mixt of 70% Na nitrate and 30% TNN was proposed in 1908 as a Mil expl (Ref 9); this was later revised to 58% Na nitrate, 27% TNN, and 15% AN. It is shock sens, can be compressed to a d of 1.4g/cc with 200 lb press, can be deton with a 0.5g MF cap, and is very hygroscopic (Ref 10). Antigrisou No 3: 82% AN, 13% Amm chloride, & 5% TNN (Ref 11, p 270). Grisounite 1: 91.5—5.5% AN & remainder TNN (Ref 11, p 276). French Mining Explosive No 1s: 95% AN & remainder TNN (Ref 11, p 277). French Mining Explosive No 3: 15% AN, 58% Na nitrate, & 27% TNN (Ref 11, p 277). Another comp of 83% AN and 17% TNN (OB to CO2 ~0.4%) is also used in mining (Ref 11, p 275). Nitroferrite: 93% AN, 2% TNN, 2% K ferricyanide, & 3% sugar is a safety mining expl (Ref 11, p 278). The following comp has been patented as mining expls: 59% AN, 13% TNN, 18% Na chloride, & 10% K perchlorate; 60% AN, 20% Na chloride, 10% TNN, & 10% gelatinized NG; and 59% AN, 18% Na chloride, 8% TNN, 5% TNT, & 10% K perchlorate (Ref 16).

It comp: Plombite: 75% Pb nitrate, 16% Ca silicide, 6.5% basic Pb carbonate, 1.5% TNN, & 1.0% vaselin was used in grenades during WW1 (Ref 36, p 342); a similar formulation of 76% Pb nitrate, 5% Ca silicide, 16% TNN, & 3% vaselin has been used as a mining expl (Ref 36, p 342). Vibrite: 78% AN, 14% Ca silicide, & 8% TNN was similarly used (Ref 36, p 353).

Jap comp: A formulization of 51.5% Amm chloride, 35.3% Ba nitrate, 8.2% of a mixt of oil and TNN, & 5.0% wood pulp was used in W WII as a booster in demolition bombs. It tends to expld when burned unconfined in large qntys (Ref 28).

1,2,5-Trinitronaphthalene (delta-Trinitro-
phthalene, 1,2,5-TNN). Colorl needles from EtOH, mp 112—13°, bp expls (Ref 3), d 1.576g/cc (Ref 32). It exists in two polymorphic forms: alpha, stable to 40°; and beta, stable above 40°. Crystallographic data for both forms are in Ref 26, p 196. It is 47.5% of the prod obtained by nitration of 1,5-DNN with mixed ac (Ref 18), and 70% of prod from nitration of 1,2-DNN with aq nitric ac for 3 hours (Ref 34). It can be sepd from comtl TNN by extn with 70% EtOH in which it is more sol (Ref 8).

1,3,5-Trinitronaphthalene (alpha-Trinitronaph-
thalene, 1,3,5-TNN). Yel rhombic crystals from chlf, mp 122—3° (Ref 2), bp expls at 364° when heated in a glass tube (Ref 12). It exists in 5 polymorphic forms, but only two are readily obtainable. Alpha 1,3,5-TNN is the form stable at room temp, but the beta form is obtained by most recrystns up to the mp. Crystallo-
graphic data on all 5 forms are in Ref 26, p 199. It is obtained, along with a small amt of TeNN and 3-nitrophthalic ac, by heating pure 1,5-DNN with concd nitric ac (45° Bé) (Ref 7); or by refluxing 1,5-DNN with 70% nitric ac for 20 hours. It is sepd from other nitrated naphthalenes by formn of a complex with beta-
naphthol, followed by chromatography (Ref 33). It gives a red color with K hydroxide in EtOH (Ref 6). Thermal analyses and mp curves for mixts of 1,3,5-TNN with a number of other nit-
trated naphthalenes are given in Ref 13.

1,3,8-Trinitronaphthalene (beta-Trinitronaph-
thalene, 1,3,8-TNN). Pale yel monoclinic cryts from EtOH, chlf, ace ct, or NB (Refs 1 & 24), mp 223° (Ref 27); crystallographic data are given in Ref 26, p 203; cryts d 1.42g/cc (Ref 23); QΟ -4223.9cal/g, QΟ -1190kcal/mole (Ref 17), QΟ -27cal/g, QΟ -1190kcal/mole (Ref 31), Qnitrat 35.28 kcal/mole (Ref 17); impact sensy similar to TNT (Ref 24), power by BalMort.
83% of TNT (Ref 24), thermal stab at 135°, no acid fumes or expn after 300 min, no extn below 360° (Ref 24); vacuum stab, 0.46cc of gas evolved/Sml of sample in 48 hours at 120° (Ref 24); hygroscopicity at 25° & 90% RH, wt gain 0.05%, at 100% RH, wt gain 0.09% (Ref 24). Its sol in a number of solvs is given in Ref 15. 1,3,8-DNN may be isolated from coml TNN in yields from 33–57%. It is best prepd by the nitratn of 1,8-DNN with concd nitric ac in sulfuric ac, yield 60%; or in aq nitric ac, yield 66% (Ref 34). It can also be prepd by the redn of 4-chloro-1,3,8-trinitronaphthalene with powd Cu in NB (Ref 13).

1,4,5-Trinitronaphthalene (gamma-Trinitronaphthalene, 1,4,5-TNN). Golden yell leaflets from nitric ac, mp 147–9° (Ref 4); QP2 = 112.7 kcal/mole (Ref 21); CA Registry No 2243-95-0. It is isolated in 3–10% yield from coml TNN (Ref 18). It is best prepd by nitratn of 1,5-DNN with nitric ac (1.5 g/cc) in sulfuric ac (1.84 g/cc) below 30°, yield 94% (Ref 33) or in good yield by nitratn of naphthalene with nitric ac in polyphosphoric ac (Ref 37). Its sol in a number of solvs is given in Ref 15.


Tetranitronaphthalenes, C10H4N2O8, mw 308.16, N 18.18%, OB to CO2 – 72.7%

Commercial Tetranitronaphthalene (TeNN). Yel cryst from acet ac, mp 200–20°, bp expl on rapid heating. It is prepd by nitratn of DNN with mixed ac whose acid concns are tabulated in Ref 8, or by nitratn of TNN with mixed ac contg an excess of oleum (Ref 12). As prepd in this way it is a mixt of isomers with the 1,3,6,8- predominating, with some 1,3,5,8- and 1,2,5,8- plus a small amt of 1,3,5,7-TeNN (Ref 17). The yield is often low due to oxidn and other side reactions, hence TeNN has not been used in expls as much as other nitrated naphthalenes, although it is similar to TNT in expl props. It has been proposed as a filler for HE Arty shells, but has not been used as such, probably because of its expense (Ref 10). A mixt of 21.5% TeNN and 78.5% AN (OB to CO2 + 0.07%) has been proposed as a HE, but there is no ref to its use as such (Ref 10). More recently workers at Katalys-Tech Chemie claimed that naphthalene can be nitrated to TeNN with mixed ac if compds of Cr, Ga, In, Mo, Ni, Ta, V,
or W are used as catalysts (Ref 13); although there has been no ref to this work in the more recent literature. The expin press of TeNN has been reported as 3745kg/sq inch at a loading d of 0.3g/cc (this d seems low) (Ref 9)

1,2,4,6-Tetranitrophthalene (1,2,4,6-TeNN). Pale yel plates from Ac_2O, mp 215\(^\circ\)C (Refs 4 & 16), decomp above its mp (Ref 16). It is prepd by nitration of 2,6-DNN with fuming nitric ac in concd sulfuric ac (Ref 16). The structure is somewhat uncertain as it was obtained in low yield. Its crystallographic props are given in Ref 16

1,2,5,8-Tetranitrophthalene (1,2,5,8-TeNN). Mp 190–2\(^\circ\)C (Ref 22). It is prepd by nitration of 1,2-DNN or 1,2,8-TNN with mixed ac at 80\(^\circ\)C (Ref 22). Its power by the Pb plate test is similar to TNT (Ref 19). The TeNN, mp 310\(^\circ\)C with decomp, which was claimed to be 1,2,5,8-TeNN (Ref 7), was later shown to be 1,4,5,8-TeNN (see below) (Ref 15)

1,2,6,8-Tetranitrophthalene (1,2,6,8-TeNN). Clusters of needles from bz/ligroin, mp 138\(^\circ\)C, decomp above its mp (Ref 16). It is prepd by nitration of 2,6-DNN with fuming nitric ac in concd sulfuric ac (Ref 22), and its crystallographic props are given in this Ref

1,3,5,7-Tetranitrophthalene (alpha-Tetranitrophthalene, 1,3,5,7-TeNN). Orange-yel bipyramids from Ac_2O, mp 260\(^\circ\)C (Refs 5 & 16), detons at 263–5\(^\circ\)C (Ref 16). It can be isolated in small amounts from coml TeNN, but is best prepd by nitration of 2,6-DNN with mixed ac at 10\(^\circ\)C, or in 42% yield by nitration of 1,2,5-TNN with excess 92.3% nitric ac at reflux for 12hours (Ref 20). Its crystallographic props are given in Ref 16

1,3,5,8-Tetranitrophthalene (gamma-Tetranitrophthalene, 1,3,5,8-TeNN). Long needles from EtOH, mp 194–5\(^\circ\)C (Ref 1), cryst d 1.54g/cc (Ref 15); CA Registry No 2217-58-5. It can be isolated from coml TeNN, but is best prepd by nitration of 1,7-DNN with mixed ac at 50\(^\circ\)C, yield 85% (Ref 16)

1,3,6,8-Tetranitrophthalene (beta-Tetranitrophthalene, 1,3,6,8-TeNN). Long needles from EtOH, mp 203.5–4.4\(^\circ\)C (Refs 2 & 24). There is no expin below 360\(^\circ\)C (Ref 14), but it exps violently on rapid heating (Ref 6); CA Registry No 28995-89-3. 1,3,6,8-TeNN is the principal component of coml TeNN and can be isolated from this source. It is best prepd, however, as follows: 1,8-DNN (10g) is added with stirring to a mixt of 50ml of fuming nitric ac (d 1.52g/cc) and 50ml of concd sulfuric ac at 20\(^\circ\)C, the mixt heated slowly to 80\(^\circ\)C over an hour and held at 80–90\(^\circ\)C for 3hours. The mixt is cooled, the solid filtered off, and the filtrate drowned in ice w. The 2 solids are combined and recrystd from 95% EtOH to give pure 1,3,6,8-TeNN (Ref 24). Qc -1082.8kcal/mole, Qf 1.5kcal/mole (Ref 15); hygroscopicity at 25\(^\circ\)C & 90% RH, wt gain is 0.07%; at 100% RH it is 0.3% (Ref 14); impact sensy is similar to Tetryl (Ref 14); power by BalMort is 101% of TNT (Ref 14); thermal stab at 135\(^\circ\)C, no acid fumes or expin after 300min; vacuum stab at 120\(^\circ\)C, 0.75cc of gas evolved/5g of sample in 48hours (Ref 14)

1,4,5,8-Tetranitrophthalene (delta-Tetranitrophthalene, 1,4,5,8-TeNN). Needles from Nb (Ref 11), stout bars (Ref 21), mp darkens ca 280\(^\circ\)C (Ref 18), melts 340–5\(^\circ\)C with decomp (Refs 3 & 11), cryst d 1.80g/cc (Ref 21); CA Registry No 4793-98-0. More recently it has been claimed that the phys props in the literature were measured on impure material and that pure 1,4,5,8-TeNN has a phase change at 270\(^\circ\)C and decomp without melting above 450\(^\circ\)C (Ref 21). Because of its high mp and thermal stab at high temps, 1,4,5,8-TeNN was examined by workers at NOL as a heat resistant exp1 (Ref 23). Below is an improved prec developed at NOL. For the prep of this compd: a mixt of 1825ml of 90% nitric ac and 1825ml of 30% oleum are placed in a 5L 3-necked flask, the mixt cooled to 20\(^\circ\)C with an ice bath, and 730g of 1,5-DNN added with stirring over 1/2hour. The mixt is stirred 1/2hour at 30\(^\circ\)C, the temp allowed to rise to 55–60\(^\circ\)C, held there until it begins to fall, then is stirred for 6/4hours. The mixt is drowned in crushed ice, the solid filtered onto a coarse sintered glass filter, the cake digested with cold w, washed again with w, and dried overnight. The crude prod is digested twice with 2L of hot ace to give 280g of crude 1,4,5,8-TeNN which can be recrystd from NB or 70% nitric ac (Ref 23, p 14). The material has the following props: Detonation velocity. In %" Al tubes, 7013m/sec (Ref 21)

Differential thermal analysis. Gives a single endotherm at 250–60\(^\circ\)C showing the above-mentioned phase transition (Ref 23, p 3)
Gas volume produced on explosion. 780cc/g (Ref 21)

**Impact sensitivity.** NOL machine with a 2.5kg wt on sandpaper gives 99cm for 50% positives (Tetryl 32cm) (Ref 23, p 3)

**Power by ballistic mortar.** 101% of TNT (Ref 21)

**Thermal stability.** It discolors without melting at 360º; on heating rapidly on a hot stage, it shows no sign of melting to 450º (Ref 23, p 2)

**Vacuum stability.** At 280º gas evolution is 0.02cc/hr at 300º 1.1cc/hr (Ref 23, p 2)

A discussion of the prep of small particle size 1,4,5,8-TeN and the reasons for its high mp and thermal stab are given in Ref 23, pp 8–12. As a prelude to its possible application in space missions, the effects of ionizing radiation on 1,4,5,8-TeN were examined by workers at PA. After 40min irradiation in a nuclear reactor (GE Test Reactor at Pleasanton, Calif), the sample became dark brown, the phase change endotherm was shifted from 270 to 291º, and a DTA exotherm occurred at 381º; after 81min irradiation the phase change endotherm came at 313º, and the exotherm at 368º. Other minor changes in props were also noted (Ref 21, p 128).


**Higher Nitrate Naphthalenes**, besides the claim by KatalystChemie, FrP 821767 (1937) & CA 32, 3964 (1938), that penta- and hexanitronaphthalene can be prep by nitration of naphthalene if certain catalysts are used, no higher nitrated naphthalenes have been reported in the literature

**Written by C. H. McDONNELL**

**Naphtalit.** A Ger chlorate expl introduced during WWI. It contained not more than 80% K chlorate and aromatic hydrocarbons (such as naphthalene), and not more than 12% nitrohydrocarbons (but no trinitro compds), the remainder consisting of paraffins, fatty oils, flour or other combustibles. It might also contain not more than 4% blasting gelatin. The prefixes Gesteins- and Wetter- were applied if the expls were intended for rock or coal mine use

**Ref:** Marshall, Dict (1920), 65

**Naphtalites.** Fr safety expls containing nitro-naphthalenes

**Ref:** Davis (1943), 157

**Naphtite.** Same as commercial Trinitronaphthalene (qv)

**Naphtites.** Expls proposed in Fr by the Société Générale Pour la Fabrication de la Dynamite, but not permitted to be manufd. These expls had properties between those of Grisoutines (see Vol 6, G143-R) and Favier (see Vol 6, F10-L ff) powders; Naphtite No 1: AN 88, NG 4 & MNN 8%; Naphtite Grisoutine: AN
92, NG 4 & MNN 4%. The first mix could not be detonated completely, even by a cap containing 1.5g of MF. Refs: 1) H. Dautriche, MP 16, 54–8 (1911–12) 2) Ibid, SS 7, 96–7 (1912)

NAPHTHOL AND DERIVATIVES

Naphthols. (Hydroxynaphthalenes; Oxy-naphthalins, in Ger). C₁₀H₇.OH, mw 144.19. Two isomers are known, 1-(or alpha) & 2-(or beta):

1(or α)-Naphthol (1-Hydroxynaphthalene).


Benzeneazonaphthol. See Benzenazonaphthol & Derivatives in Vol 2, B53-R ff

Benzeneazonitronaphthol. See Benzenazonitronaphthol & Derivatives in Vol 2, B54-R ff

1-Naphthol Additive Compounds

2,4,6-Trinitro-3-Methyl-Phenol + 1-Naphthol (2,4,6-Trinitro-m-cresol + 1-oxy-naphthalene). HO.(O₃N)₃C₆H₃.CH₃ + C₁₀H₇.OH, mw 387.33, N 10.85%, OB to CO₂ -142.51%, orange-yellow silky needles from dil alc, mp 159°. Sol in hot alc. Prepn by mixing hot saturated alc solns of the constituents & allowing the mix to cool slowly. Explan temp 472°. Ref: Beil 6, [578] & [2922]


2-Naphthol Additive Compounds

2,4,6-Trinitro-3-Methyl-Phenol + 2-Naphthol (2,4,6-Trinitro-m-cresol + 2-Oxy-naphthalene). HO.(O₃N)₃C₆H₃.CH₃ + C₁₀H₇.OH, mw 387.33, N 10.85%, OB to CO₂ -142.51%, orange needles from dil alc, mp 124°. Sol in hot w & dil alc. Prepn by mixing hot saturated w solns of the constituents & allowing the mix to cool slowly. Explan temp 452°. Ref: Beil 6, [597] & [2969]

Mononitrocompounds of Naphthols

Only one of these compounds decomp at its mp:

Other Derivatives of the Mononitrocompounds of Naphthols

1-Nitro-4,6-Dibromo-2-Naphthol (4,6-Dibromo-1-nitro-2-naphthol). Br₂C₆H₄(NO₂)OH, mw 346.97, N 4.04%, OB to CO₂ 89.99%, yellow needles from alc, mp 148–50° (decompn). Prepn from 4,6-dibrom-2-naphthol by nitrification with nitrous-nitric acid (d 1.5g/cc) in AcOH at RT
Ref: Beil 6, 609

2-Nitro-4-Iodo-1-Oxy-Naphthalene (2-Nitro-4-iodo-1-naphthol). (O₂N)C₆H₄(OI)OH, mw 315.09, N 4.45%, OB to CO₂ 101.56%, clear golden needles, mp 115° (decompn). Prepn from 4-nitro-2-acetoxymercuric-naphthol-(1) by reacting with iodine
Ref: Beil 6, (586)

1-Nitro-3,4,6-Tribromo-2-Naphthol (1-Nitro-3,4,6-tribromo-2-oxy-naphthalene). O₂N.C₆H₃Br₃OH, mw 425.87, N 3.29%, OB to CO₂ 71.38%, turns black at 135°, mp 136° (decompn). Prepn from 1,3,4,6-tetrabromo-1-nitro-2-naphthol by reaction with nitric acid, then alkali
Ref: Beil 6, 655

Dinitrocompounds of Naphthols

Dinitro naphthols. (O₂N)₂C₆H₄OH, mw 234.17, N 11.96%, OB to CO₂ 123.00%

2,4-Dinitro-1-Naphthol (2,4-Dinitro-1-oxy-naphthalene). Yellow crystals, mp 139.5°. Sol in alc & chl. Prepn from naphthalene as a by-product during nitrification with dil nitric acid & Hg(II) nitrate. The Lead Salt of the above can be shown as Pb[(O₂N)₂C₆H₄(NO₂)₂]₂, mw 729.57, N 7.68%, OB to CO₂ 76.75%. The explosive sensitivity of this salt compared to PA is 49%

4,5-Dinitro-1-Naphthol (4,5-Dinitro-1-oxy-naphthalene). Yellow needles from alc, mp 208° (decompn). Sol in alc, acet, alkaline & ammoniacal w soln; sl sol in w. Prepn from 5-nitro-naphthochinon-(1,4)-oxime (4) by reacting with basic K ferrocyanide soln at RT

4,6-Dinitro-1-Naphthol (4,6-Dinitro-1-oxy-naphthalene). Crysts from methanol (as Na salt), mp 240°. Sol in chl. Prepn from 1,4,6-trinitro-2-naphthylamine by diazotization in AcOH-sulfuric acid to yield 4,6-dinitro-2-diazo-1-naphthol; steam is passed thru the mixt to yield the naphthol

4,8-Dinitro-1-Naphthol (4,8-Dinitro-1-oxy-naphthalene). Yellow needles from 25% alc/w; mp, turns black at 200° & melts at 235° (decompn). Sol in alc, AcOH & cold Na carbonate soln. Prepn from 8-nitro-naphthochinon-(1,4)-oxime-(4) by oxidation with alkaline K ferrocyanide
Ref: Beil 6, 619


1,6-Dinitro-Naphthol (1,6-Dinitro-2-hydroxy-naphthalene). Pale yellow needles from chl, mp 195° (decompn). Sol in eth, hot alc, chl & py. Prepn from bis-(2-hydroxy-1-naphthyl) sulfide by nitrification in AcOH at 55°. Yield 78%

1,8-Dinitro-2-Naphthol (1,8-Dinitro-2-oxy-naphthalene). Brownish yellow leaflets or needles from alc, mp 198–99° (decompn). Sol in w, alc & chl. Prepn from 1,8-dinitro-2-ethoxy-naphthalene by heating with alc KOH
Ref: Beil 6, 655–56, (316) & [610, 656]

4,5-Dinitro-2-Naphthol (4,5-Dinitro-2-oxy-naphthalene). Mp 238°. Prepn from 4-nitro-2-naphthyl-m-nitrobenzenesulfonate by nitrification & hydrolysis with piperidine
Trinitro-1-Naphthols

(O₃N)₃C₁₀H₄OH, mw 279.17, N 15.05%, OB to CO₂ – 88.50%. All of the trinitro naphthols expel on heating. Some of their salts are also expl

2,4,5-Trinitro-1-Naphthyl (2,4,5-Trinitro-1-hydroxy naphthalene). Yellow leaflets or prisms; mp 189–90°; bp, explds. Sol in hot AcOH, sl sol in hot w, alc, benz, eth acetate, xylene & cold AcOH. Prepn from 2,4-dinitro naphthyl by nitration, or from 4-chlor-1,3,8-trinitronaphthalene by heating with 0.1N NaOH in w or alc


2,4,7-Trinitro-1-Naphthol (2,4,7-Trinitro-1-oxy naphthalene). Yellow prisms from AcOH or benz, mp 145° (decomp). Sol in AcOH & glc AcOH. Prepn from 2,4-dinitro-1-naphthol by mixed acid (nitric-sulfuric-acetic) nitration. The compound is extracted as the Na salt from the AcOH washings of the concd mother liq


2,4,8-Trinitro-1-Naphthol (2,4,8-Trinitro-1-oxy naphthalene). Yellow prisms, mp 175°. Sol in cold w. Prepn from 8-nitro-naphthoquinone-(1,4)-oxime by heating with dil nitric acid

Refs: Beil 6, 620 & (309)

2,4,6-Trinitro-5-Acetoxy-1-Naphthol (2,6,8-Trinitro-5-hydroxy-1-acetoxy-naphthalene, acetic acid-[2,6,8-trinitro-5-hydroxy-1-naphthyl-ester], [2,6,8-trinitro-5-hydroxy-1-naphthyl-acetate]. (O₃N)₂C₁₀H₃(OOCCH₃),OH, mw 337.22, N 12.46%, OB to CO₂ – 87.78%, yellow needles from AcOH, mp 223° (decomp). Prepn from 1,5-diaceoxy-naphthalene by nitration with dil nitric acid at 40–50°

Refs: Beil 6, (5275)

X,XX-Trinitro-3-Chlor-1-Naphthol (X,XX-Trinitro-3-chlor-1-oxy-naphthalene, X,XX-trinitro-4-chlor-2-oxy-naphthalene). (O₃N)₂C₁₀H₃ClOH, mw 313.62, N 13.40%, OB to CO₂ – 76.53%; crystals from AcOH with 1 mol AcOH as yellow-blue needles, mp ~156°
(decomp). Sol in alc & AcOH. Prepn from 1,3-dichlor-X,X,X-trinitro-naphthalene by heating with alcoholic NaOH
Ref: Beil 6, 664

**Trinitro-2-Naphthols**

1,6,8-Trinitro-2-Naphthol (1,6,8-Trinitro-2-hydroxy naphthalene). Light yellow crystals, mp 221°. Prepn from 7-chlor-1,3,8-trinitronaphthalene by treating with NaOH soln in the presence of acet. Expdls on heating
**Refs:** 1) Beil 6, (610) 2) E.J. van der Kam, Rec 46, 725 (1926)

X,4,6-Trinitro-2-Naphthol (X,4,6-Trinitro-2-oxy-naphthalene). Yellow needles from alc, mp 150° (decomp). Prepn from 4,6-dibromo-2-naphthol by nitrilation with nitrous-nitric acid. Rapid decomp occurs above 159°
Ref: Beil 6, [610]

X,X,X-Trinitro-7,8-Dinitroso-2-naphthalene (7,8-Dinitroso-X,X,X-trinitro-2-oxy-naphthalene). (O₂N)₃C₁₄H₂(NO)₂OH, mw 337.18, N 20.78%, OB to CO₂ = 59.21%, yellow crystals, mp 208° (decomp). Prepn from an AcOH suspension of 7-oxy-naphthochinon-(1,2)-dioxime by heating with nitric acid. Expdls when heated above mp. The mono K salt (orange yellow crystals) expdls with great violence when heated to about 260°. This salt, together with the Pb salt of trinitro-phenyl-glucinol, has been used as a priming comp for loading blasting caps, Flobert ammo & the like
Ref: 1) Beil 8, 300 2) H. Rathbusch, Brit P 190215 (Sept 10, 1921) & CA 17, 3101 (1923)

**Tetranitro-1-Naphthols**

(O₂N)₄C₁₄H₂O₇, mw 324.18, N 17.29%, OB to CO₂ = 64.20%

2,4,5,7-Tetranitro-1-Naphthol (2,4,5,7-Tetranitro-1-hydroxy naphthalene). Mp 180°, yellowish leaflets or needles. Sol in cold AcOH, better in hot AcOH; sl sol in benz (1p in 220p benz at 18°). Prepn from 4-brom-1,3,6,8-tetranitro naphthalene by heating on a w bath with an excess of Na carbonate soln. Expdls on heating. Forms some expl salts
Ref: 1) Beil 6, 620 2) V. Merz & W. Weith, Ber 15, 2714 (1882)

4,4,4,4-Tetranitro-1-Naphthol (4,4,4,4-Tetranitro-1-oxy-naphthalene). Yellow needles from alc, mp 215°. Prepn from 4-nitro-1-ethoxy naphthalene by nitration
Ref: Beil 6, 621

X,X,X,X-Pentanitro-X-Naphthol (X,X,X,X-Pentanitro-X-oxy naphthalene). (O₂N)₅C₁₄H₂.OH, mw 369.18, N 18.97%, OB to CO₂ = 45.51%. Prepn from naphthalene by action of nitric acid & Hg nitrate followed by sulfuric acid
Ref: 1) Beil - not found 2) T.L. Davis, USP 1419027 (1922) & CA 16, 2781 (1922) 3) A.H. Blatt & F.C. Whitmore, OSRD 1085, 74 (1942)

**Nitrosocompounds of Naphthols**

There is only one nitroso compound that decomp at its mp:

4-Nitroso-1-Naphthol (Naphthochinon-(1,4)-monoxime). ONC₁₄H₈O₅, mw 173.18, N 8.99%, OB to CO₂ = 198.64%, pale yellow needles from benz or dil alc, mp 193–94° (decomp at 190° thru mp). Sol in alc, me alc, acet, eth, clfl & C disulfide. Prepn from 4-nitrosomethoxy-naphthalene by saponification with mineral acid. Qₓ = 1166.4cal/g-mole & Qᵧ = 1166.5 cal/g-mole

**Peroxides of Naphthols**

There is only one peroxide compound that expdls (by rubbing):

7-Hydroxy-1,2-Dioxo-1,2-Dihydro-Naphthalene (7-Hydroxy-naphthochinon-(1,2), 7-Hydroxy-1,2-naphthoquinone). (HO).C₁₄H₂(O)₂, mw 224.16, OB to CO₂ = 183.74%, dark red microcrysts, mp 203–204° (decomp). Sol in alc & AcOH. Prepn from 1-amino-2,7-dioxo-naphthalene by oxidation with chromic-sulfuric acid
Ref: 1) Beil 8, 299, (634) & (2542) 2) S. Mededeco & O. Bloch, ChemZtr (1935), 2670 3) Tobolsky & Mesrobian (1954), 179

**Dihydroxynaphthalene and Derivatives**

Note: These compounds are described in Vol 5, D1294-L to D1295-L, however, more recent edi-
tions of Beil have revealed several additional derivatives, two of which are of particular interest:

$\pm$-1,3,5,6-Tetramethyl-1-Nitroxy-1H-Naphthalendiol-(2,2) ($\pm$-1,3,5,6-Tetramethyl-2,2-dihydroxy-1-nitroxy-1,2-dihydroxynaphthalene, $\pm$-1,3,5,6-tetramethyl-1-nitroxy-naphthalene-2,2(1H)-diol).

\[
\begin{array}{c}
\text{Br} \\
\text{O} - \text{NO}_2 \\
\text{OH} \\
\text{OH} \\
\text{Br} \\
\end{array}
\]

mw 538.78, N 2.60%, OB to CO$_2$ -51.97%, needles from benz, mp 121$^\circ$ (decomp). Sol in benz & alc. Prepn from an AcOH suspension of 1,3,5,6-tetramethyl-2-naphthol by warming with dil nitric acid (d 1.4g/cc).

Ref: Beil 7, (3693)

2-Nitroso-Naphthalendiol-(1,8) (2-Nitroso-1,8-dioxynaphthalene). ON.C$_1$OH$_2$.OH$_2$, mw 189.18, N 7.41%, OB to CO$_2$ -173.38%, brownish yellow needles from benz; mp, turns dark at 170$^\circ$ & decomp at 183$^\circ$. Sol (exhibiting a yellow color) in acet, eth, alc, lgr & benz. Prepn from 1,8-dioxy naphthalene by reaction with Na nitrite in AcOH. Explsds when heated quickly.

Ref: Beil 8, [344]

**Written by: H. L. HERMAN**

**Naphthylamines.** See under Aminonaphthalenes and Derivatives in Vol 1, A237-L to A238-L.

**Nationalite.** A Brit coal mine expl of the Grisonvntite class (see Vol 6, G-143-L). The original composition contained AN 92 & Di- and Trinitrotoluenes 8%. In order to pass the Rotherdam Test for acceptance on the permitted list, it was necessary to add alkali chlorides, resulting in the following formulations:

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<th>No 2</th>
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<td>1-28-1915</td>
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<td>TNT, %</td>
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<tr>
<td>Power (BarPend swing, inches)</td>
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</table>

The permits were subsequently repealed.

Ref: Marshall, Dict (1920), 65

**National Transportation Safety Board.** An independent agency of the US Government established under the Transportation Safety Act of 1974, reporting directly to the Congress with recommendations for legislation. It conducts a continuing review of safety in all modes of transportation, including hazardous materials. Thru its Hazardous Materials Safety Division, the Board evaluates the adequacy of safeguards and procedures concerning the transportation of hazardous materials as well as the performance of other government agencies charged with assuring the safe transportation of such materials. Although the Board has no regulatory authority, their recommendations and responses to these recommendations are published in the Federal Register.

Ref: J. H. Reed, “Hazardous Materials Safety — Where Are We Going?” Transportation Association of America National Seminar, Denver, Colorado (June 1975)

**Natrimatrite No 19.** See under Almatrites in Vol 1, A140-L.

**Natural Barricade.** See under Barricades in Explosives and Ammunition Installations in Vol 2, B22-R.

**Natural Gas.** See under Gas, Natural in Vol 6, G27-R. Dangerous fire and expln hazard. Flash pt 900–1170°F; flammable limits in air 3.8–6.5% & 13–17% by vol (Ref 2). Stoichio-
metric natural gas-air mixts were exploded at pressures as low as 0.2 atm in a pipe 2 ft in diameter by 300 ft long. Measured explnt pressures exceeded the theoretically predicted pressures of a detonation. The detonation hazard can be reduced by the proper application of water sprays in the region in which the detonation is being developed. The combination of water sprays and a large increase in the vel of the system stopped the established detonation (Ref 1).


**Nauchoff’s Explosives.** Low freezing plastic expls patented prior to WW1 by S.A.S. Nauchoff of Sweden. It was claimed that they were equal to Dynamites in performance. Examples are: (1) Liq TNT (gelatinized by dissolving 4p of NC in 96p of liq TNT, called "flüssige Tri" in German) 31, Amm perchlorate 43 & AN 26% (Ref 3); (2) Liq TNT (gelatinized) 31, AN 43 & Na nitrate 26% (Ref 1); and (3) Liq DNT (gelatinized) 31, Amm perchlorate 43, & Na or K nitrate 26% (Ref 2). One of these expls was called Territ (qv)

Refs: 1) S.A.S. Nauchoff, USP 1058891 (1913) & CA 7, 1975 (1913)
2) Ibid, USP 1061774 (1913) & CA 7, 2309 (1913)
3) Colver (1918), 247 & 681

**Navez Chronograph.** See under Chronographs, Chronoscopes, Chronometers and Other Devices Used in Measuring Velocities of Projectiles in Flight and of Detonation Velocities of Explosives in Vol 3, C305-R

**NBSX or ATX.** Code designations for 1,7-Dinitroxy-1,3,5,7-tetramethylene-2,4,6-trinitramine or 1,7-Dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, described in Vol 5, D1295-R

**NC.** Abbr for Nitrocellulose

Ref: Anon, OrdTechTerm (1962), 202-R

**N.E.** Brit sporting smokeless propint introduced in 1912. It contains NC (insol) 50.0, NC (sol) 25.8, metallic nitrates 12.0, nitrohydrocarbons 7.0, vaseline 3.5 & moisture 1.7%

Ref: Marshall 3 (1932), 96

**Nebelwerfer.** Ger for "smoke thrower". A WWII Ger artillery piece that was originally designed to launch smoke shells, but was modified to launch rockets, including 150mm, 210mm and 320mm types. As many as six launchers were mounted on one vehicle. The total weight of the 150mm unit was about 1200 lbs, and the rockets had a range of up to 7750 yds. Nebelwerfer were first used on the Russian front in 1941

Refs: 1) Anon, OrdTechTerm (1962), 202-R

**Neck.** Cylindrical portion of cartridge case between mouth and shoulder (Ref 1). The part of a cannon immediately behind the swell of the muzzle (Ref 2)

Refs: 1) Anon, OrdTechTerm (1962), 202-R

**Needle Gun.** A gun that utilizes a needle-fire cartridge in which a needle penetrates thru the base of the cartridge and strikes the primer within the case, thus setting off the charge. Needle guns were of muzzle-loading and breechloading types, the best known of the latter being the Dreyse rifle, which was first used by the Prussians (see under Johann Nicolas von Dreyse in Vol 5, D1544-R). It was a single-shot rifle with a bolt-breech action, and fired a conical
bullet encased in a paper cartridge with a powder charge. The bolt of the rifle contained a long needle that penetrated the paper cartridge, passed thru the propit, and detonated a primer attached to the base of the bullet. This weapon, in .607 cal, was adopted by the Prussian Army in 1840 and remained in service thru the wars with Austria (1866) and France (1870). Other needle guns included the Chassepot (see in Vol 2, C154-L), Needham and Chateauvillard


**Ref:** Anon, “Military Explosives”, TM 9-1910 (1955), 214

**NENA.** Code name for N-(β-Nitroxyethyl) nitramine. It is described as 1-Nitramino-2-ethanol Nitrate in Vol 1, A201-L. See also MeNENA and Me₂NENA in this Vol, EtNENA in Vol 6, E342-L, and Iso-Me-NENA in Vol 1, A253-L

**NENO.** Code name for N,N'-Dinitro-N,N'-bis (2 hydroxyethyl)-oxamide Dinitrate (CA nomenclature). See in Vol 5, D1244-L to D1245-R

**Addnl Ref:** A.J. Phillips, “Suitability of NENO as a Military Explosive”, PATR 1441 (1944)

**Néo (Poudres).** Fr double-base propitns containing diethyleneglycoldinitrate (DEGDN) and nitrocellulose

**Neonals.** Brit permissible expls; **No 1:** K perchlorate 14, NG 40, collodion cotton 2, woodmeal 4.5, Amm oxalate 39.5 & w 0.5%; power by BalPend 2.51", limit charge 30 oz; **No 2:** K perchlorate 37, NG 21, collodion cotton 1, TNT plus DNT 0.2, woodmeal 15, Amm oxalate 25 & w 0.8%; power by BalPend 2.56", limit charge 16 oz

**Refs:** 1) Marshall 1 (1917), 385 2) Barnett (1919), 137

**Neonite.** A fast burning, 30 grain, gelatinized smokeless powder introduced in 1907 by the New Explosives Co of Eng. It contains NC (insol) 73.0, NC (sol) 9.0, metallic nitrates 10.5, vaseline 5.9 & moisture 1.6% (Ref 1)

The same name was also given to a single-base propit, designed for small arms, developed by I.C.I. Ltd (Ref 2). The required ballistics for different types of ammo are obtained by surface treating the propit grains with methyl centralite, and in some cases, dibutyolphthalate.
The coating penetrates into the base grain to some extent to give, in effect, a progressively increasing rate of burning as the grain burns away.


Neopenteryl. 2-Nitro-2(3',5'-dinitrophenyl)-propane-diol-1,3-Dinitrate. Its power is reported as 133% of TNT.

Ref: D.P. MacDougall et al, OSRD 5746 (1945), 18

Neptune Powder. American expl prep by A.J. Parker about 1878. It contains NG 33, NaNitrate 45, charcoal 17 & sulfur 5%.

Ref: Van Gelder & Schlatter (1927), 619

Neu-Babelsberg Calorimeter. Apparatus constructed by Zentralsstelle für Wissenschaftlich-technische Untersuchungen G.m.b.H. at Neu-Babelsberg, near Berlin, in Ger, was used for the determination of heats of combustion of expls.

Ref: Colver (1918), 615

Neudynamits. Austrian term for gelatin Dynamites. There were two types used: (1) NG (gelatinized) 66.00, K nitrate 24.82, woodmeal 8.84 and soda 0.34% (2) NG (gelatinized) 45.00, K nitrate 40.15, cereal meal 14.30 and soda 0.55%.

Ref: Naoum, NG (1928), 329

Neugen. Polyethylene glycol laurate; used as an additive to prevent the expl reaction of Bazide. See under Barium Diazide in Vol 1, A524-L.

Neumann, Egon (1884–1919). German ballistician & armament technologist. Especially known as a co-discoverer of the shaped charge or cavity effect, also known as the Munroe-Neumann Effect (See Munroe Effect; Detonation, Munroe-Neumann Effect, or Shaped Charge

Effect in Vol 4, D442-R to D454-L). This discovery, at a somewhat later date in Germany than in the USA (1910 for Neumann vs 1888 for Munroe), has been shown to be independent of the work of Munroe. Engineer, inventor, author, lecturer and well-known authority on explosives, his work, both basic & applied, covered many phases of the armament industry.

Refs: 1) E.G. Neumann, GerP AmmW 36269 (1910) 2) E.G. Neumann, BritP 28030 (1911) 3) E.G. Neumann, ZAngewChem, 2238 (1911) 4) E.G. Neumann, SS 12, 183 (1914) 5) Anon, SS 17, 293 (1919) 6) Davis (1943), 20 7) Cook (1958), 226


Neu-Nobelit. (New Nobelite). Semi-plastic permissible expls which were used in Ger coal mines during the shortage of NG in and following WWI. However, for work with accompanying rock, the stronger gelatin permissible with 25 to 30% NG were preferred. One of the later types of Neu nobelits was No XVI: NG 12, AN 54, woodmeal and coal 3, nitrocompounds 3 and alkali chlorides 28%. Its properties were: OB to CO2 +2.9%, Trauzl block expansion 225.0cc, Pb block crushing 13.0mm, vel of deton 4600m/sec, Qe 643.00cal/g, temp of expl 1828°

Refs: 1) Naoum, NG (1928), 441 & 444 2) PATR 2510 (1958), Ger 117-L

Neutral Propellant Grain. A single piece of propellant that maintains its burning surface constant, or approximately constant, during burning is said to have neutral geometry. Simple neutral geometries include sheets, squares or disks with webs small compared with surface dimensions, or with edges inhibited; long tubes, or tubes with ends inhibited. See also under Cannon Propellant in Vol 2, C31-L


Neutron Kill. A method of destroying objects, including enemy nuclear warheads in the atmosphere,
by means of a nuclear detonation. The *Sprint* interceptor missile of the *Safeguard ABM* program is intended to destroy incoming warheads by means of the neutron effect of its 1–2 kiloton warhead as well as by blast. The neutron emission of the interceptor’s warhead is intended to trigger fission within the enemy warhead, thus generating very high temps which damage the warhead and prevent a normal detonation

**Neutron Radiation.** See under Radiation Effects on Explosives, Propellants and Pyrotechnics

**Neuwestfalit.** A Ger Favier-type permissible expl contg AN 70.3, DNT 10.9, Na chloride 16.8 & flour 2.0%. Trauzl test value 309cc; charge limit 540g

**New Explosive Co., Ltd.** At Stowmarket, Engl., it was the first plant to manufacture compressed blocks of wet NC by Abel’s method. These blocks were used as bursting charges in various projectiles as well as for demolition purposes. This facility also manufd Dynamites, Gelignite, Cordite, Carbonite, etc
*Ref*: Daniel (1902), 451

**New Fortex.** See under Fortex in Vol 6, F174-L

**Newt.** A Rus pre-WWI mining expl contg NG (gelatinized with collodion cotton) 4, AN 78, Knitrate 5, Na chloride 8 & vegetable meal 5%
*Ref*: Anon, SS 12, 431 (1917)

**Newton Powder (Saxifragine).** Belgian blasting expl patented in 1862 contg Ba nitrate 77, charcoal 21 & K nitrate 2%
*Ref*: Daniel (1902), 701

**NG.** Abbr for Nitroglycerin

**NGK.** Abbr for Nitroglycol

**NGu.** Abbr for Nitroguanidine

**NGX.** Code name for 1,2,3-Trinitroaminopropane

**N.H. Powders.** Abbr for nonhygroscopic powders

**N-HMX.** Code name for 1-Nitroso-3,5,7-trinitro-1,3,5,7-tetra-azacyclooctane

**Nib.** Abbr for Nitroisobutyl

**NIBGTN.** Abbr for Nitroisobutylglycerol Tri-nitrate

**Nickel.** Ni, at wt 58.71, at no 28, valences +2 & +3, five stable isotopes, 7 radioactive isotopes. Malleable, silvery metal; readily fabricated by hot and cold working; takes high polish; excellent resistance to corrosion. Mp 1455°; bp 2900°; d 8.908g/cc; electrical resistivity (20°) 6.844 microhm-cm; Moh’s hardness 3.8; spec heat (100°) 0.1123; latent heat of fusion 73cal/g. Stable in air at ordinary temps; burns in O₂ forming NiO; not affected by w; decomps steam at red heat. Slowly attacked by dil hydrochloric or sulfuric acids; attacked by nitric acid. Not attacked by fused alkali hydroxides (Refs 5 & 6). The most comprehensive and modern monograph on Ni and its compds is Gmelin (Ref 3)
Ni is found in many ores in combination with S, As & Sb, the chief sources being the minerals chalcopyrite, pyrrhotite and pentlandite. Ni ores are of two types, sulfide and oxide, the former accounting for two-thirds of the world’s consumption. Sulfide ores are refined by flotation and roasting to sintered Ni oxide, and either sold as such or reduced to metal, which is cast into anodes and refined electrolytically or by the carbonyl (Mond) process. Oxide ores are treated by hydrometallurgical refining, eg. leaching with ammonia. Much secondary Ni is recovered from scrap (Refs 6 & 7)
Probably the largest use of Ni is in the manuf of Monel metal, stainless steels, Ni-chrome resistance wire, in alloys for electronic and space applications, and as a catalyst (Raney Ni). It is also used as a fuel in pyrotechnics (Ref 2) and in delay powders as a Zr alloy (Ref 4).

Exposure to Ni may cause dermatitis (Ni itch) in sensitive individuals. Ingestion of large amounts (even 1-3mg/kg of body wt) causes nausea, vomiting, diarrhea, & depression of the central nervous system. Its health hazard is, however, considered slight. The M.A.C. (max allowable concen based on continuous exposure for an 8 hr day) is 0.5 mg/cu m (Refs 2 & 5)

Ni dust is expl and a dangerous fire hazard. It has an ignition temp above 700°, and burns with intense heat. When compounded with oxidizing agents, the powdered metal is a dangerous fire and explosion hazard. The amt of powdered metal which may become involved in a fire should be strictly limited. Fires must not be fought with ordinary streams of water because of the danger of liberating large quantities of hydrogen gas. Fires involving small amts of powdered Ni may be fought with fog nozzles or special extinguishing powders (Ref 2).

The requirements for the US Armed Forces are detailed in the JAN Spec listed as Ref 1, which covers powdered Ni suitable for use in ammo. It specifies the following requirements:

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free metallic nickel</td>
</tr>
<tr>
<td>Mercury</td>
</tr>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>Granulation</td>
</tr>
<tr>
<td>Average particle diam</td>
</tr>
</tbody>
</table>


Nickel-Hydrazine Nitrate Complex. Ni(NO₃)₂·3N₂H₄; rose-lilac colored crys powder; degrades at 212-15°. Prepd by pouring slowly with stirring a 20-30% aq or alc soln of Ni nitrate into a 40% alc soln of hydrazine maintained at 10-20° until 4-5% excess hydrazine remains. The ppt is immediately filtered, washed thoroughly with MeOH or EtOH to remove excess hydrazine; and dried at 100° in a steam oven. It has a drop sensitivity of about 1.4m with a 2kg wt. In the Pb block test it gave a coeff utilisation pratique of 87.7 & 85 (PA=100). In cellophane tubes 200mm long at d=0.62g/cc with a 0.4g MF detonator, the vel of deton by the Dautriche method for various tube diameters were: 2600m/sec at 6mm diam, 2900 & 3100 at 8mm, 2700 at 10mm, 2900 at 12mm, and 3500 at 15mm. It is not easily detoned by flame or heat in 2 to 2.5g charges even when mixed with Pb styphnate, Pb picate or powdered Hexogen. In trying to improve the ignition quality, Ni styphnate-hydrazine complex was prepd and found more ignitable, with a drop sensitivity of about 2.6m with a 2kg wt Ref: L. Méard & J. Barlot, MP 34, 160–66 (1952) & CA 48, 6125 (1954)

Nickel Powder. Expl patented in 1889 in Engl by
Liardet and authorized for use in Australia. It was prepd by dissolving PA in half its weight of hot glycerin, and incorporating woodmeal and K nitrate
Ref: Daniel (1902), 406

Niepce’s Incendiary Composition. Contained benz, petroleum or carbon disulfide with a small piece of metallic potassium or Ca phosphate as igniter. Potassium was later replaced with metallic sodium
Ref: Daniel (1902), 153

Nightingale and Pearson Powder. Mining expl patented in Engl in 1897. It contained K perchlorate 55–60, Na carbonate 25–29, sugar 6–10 and paraffin 5–20%. Potatoes or woodmeal could replace the sugar
Refs: 1) Daniel (1902), 452 2) Pérez Ara (1945), 212

Nigrasine. A dye consisting of a mixt of aniline, aniline hydrochloride and nitrophenol, or nitro-benzene and Fe. It was used in Ballistite proplnts in 0.05–0.10% concn (see under Ballistite in Vol 2, B9-R)
Refs: 1) F.M. Rowe, “Colour Index”, The Society of Dyers and Colourists, 1st Ed (1924), 216 2) L. Pauling, OSRD 3783 (1944)

Nike. Name applied to a system of US Army surface-to-air guided missiles designed to seek out, intercept, and destroy enemy aircraft. The Nike-Ajax was the first US operational supersonic antiaircraft guided missile. First deployed in 1953, it had a length of 31 ft (with booster), a launch wt of 2300 lbs, a ceiling of 60000 ft, and a range of 25 miles. Its successor, the Nike-Hercules, became operational in 1958. It had a length of 39 ft (with booster), a launch wt of 10000 lbs, a ceiling in excess of 150000 ft, and a range of over 75 miles. The Nike-Zeus increased the range to about 200 miles at an estimated speed of Mach 4. The Nike-X is the latest antimissle-missile system for defense against ballistic missiles, and a follow-on to Nike-Zeus. The system includes a multifunction array radar which performs target acquisition, discrimination, and tracking functions; a missile-site radar which performs missile command, target track and search functions; data processing equipment consisting of high speed digital computers; and Sprint missiles

Nikles. Proposed an incendiary cmpn, called “feu lorrain”, consisting of hydrochloric and sulfuric acids, and a soln of phosphorus in carbon disulfide. The mixt ignites, evolving heavy reddish fumes, when brought in contact with an ammoniacal soln
Ref: Daniel (1902), 154

Nilite. Trademark for a series of DuPont Co nitrocarbonate blasting agents

Niperit (Niperith, Niperyth). Same as PETN

Nipolite (Nipolite). A propInt or expl cmpn developed during WWII at the Kraiburg plant of the Deutsche Sprengchemie GmbH. Two comprs are reported: Nipolite (tubes) contain PETN 35, NC (12.6% N) 34.1, DEGDN 30, stabilizer 0.75, Mg oxide 0.05 & graphite 0.1%. Nipolite (sticks) contain PETN 50, NC (12.6% N) 29.1, DEGDN 20, stabilizer 0.75, Mg oxide 0.05 & graphite 0.1%. Nipolite is prepd by air-agitating a w slurry of NC and DEGDN in a Pb-lined vessel. After 15–20 minutes stirring, the mass is centrifuged to remove all but 25% of w. The resulting cake is kneaded at 50° in a Werner-Pfleiderer machine with the calculated amt of PETN, some w, Mg oxide and graphite. After 15 minutes of kneading, the paste is transferred to rubber-lined bags where it is allowed to age for 48–72 hrs. The aged paste is then passed 15–20 times thru a pair of vertical rollers maintained at 75° to produce a
sheet which is later extruded at a pressure of 200 kg/sq cm and temp of 80°. The resulting tubes or sticks are then cut into desired lengths.

In using Nipolit, the "stick" is wetted with acetone and pushed into the "tube", of such a length that one end is flush, leaving a cavity in the other end to accommodate a detonator. This assembly was used as a booster charge in ammo (Refs 4 & 5).

As Nipolit-type expls were of interest to the US Ordn Corps, a study was initiated to modify the Ger manuf process which was considered to be hazardous because of the heated roller treatment. A new compn was developed consisting of RDX 35.9, NC (12.6% N) 24.5, NG 22.8, DNETb, 10.0, DBuPh 6.6 & DPhA 0.2%. It was tough and thermally stable, relatively non-lygroscopic, and insensitive to friction, impact and rifle fire. It was also superior to TNT in rate of detonation and brisance. A relatively simple and non-hazardous procedure was developed for its manuf. Another formulation variation was TNT 35, Comp A: 35, M-1 proplnt powder 20, and DNETb or TEGDN 10%. This was hard and tough at room temp, but softened at 65° (Refs 1 & 3).

Extrudable Nipolit-type expls were developed at PiCaRsn for use in the development of caseless bombs (Ref 2). Typical formulations contain RDX/Resin 83/17 and RDX/Al/Resin 80/10/10 or 60/23/17. Three resins, Marco MR-280, Laminac 4116 and Selectron 5003, were found to be satisfactory and interchangeable for use in these comps. These expls are thermally stable, relatively insensitive to mechanical shock, and have a brisance approaching that of Comp C-3. Weight-drop impact tests indicate them to be of the order of sensitivity of TNT.


Nisser Powders. One of the early perchlorate expls, patented in 1865, contg K perchlorate 10.5, K nitrate 44.5, K dichromate 2.0, K ferrocyanide 1.5, charcoal 19.6, sulfur 15.5 and sawdust 6.5% (Ref 2). Nisser also patented in 1870 a mixt contg a chlorate, K ferrocyanide, K bitartrate and charcoal (Ref 1).

Refs: 1) Daniel (1902), 452 2) Pérez Ara (1945), 219

Nital. A soln of 1-5 ml of nitric acid (d 1.42 g/cc) in 100 ml of 95% alc, used for etching metals. A nital soln contg about 15% by vol of Grasselli reagent, nitric acid and ethanol, used for etching Bi, decomposed vigorously. Explns were also reported when nital mixt came in contact with other metals. It is believed that the decomn was caused by the reduction of the nitric acid to oxides, which catalyzed the decomn (Ref 1).

A possible additional cause is the formation of a highly unstable salt, similar to fulminate, by the action of nital on metals. In order to prevent future incidents, it is recommended that methanol be used in lieu of ethanol in nital mixts (Ref 2).


Niter. Same as Potassium Nitrate

Niter Cake. Same as Sodium Bisulfite

Nitrat. Fr designation for Tetramethylammonium Nitrate. It is called Tetrazel in Ger Ref: A. LeRoux, MP 35, 121-32

Nitramex. Trademark for an AN based blasting agent developed by the duPont Co for use in dynamiting very hard rock, in quarry work, and in stripping operations where the toe is difficult to break. It is not detonated by rifle bullet impact, sledge hammers or heat, but rather by specially constructed primers. Nitramex is stronger and denser than Nitramon (see in this Vol), another duPont Co commercial blasting agent.


Nitramides. Expls similar in composition to
Favier expls described in Vol 6, F10-Lff. Also see under Amides and Imides, Organic, Nitratred in Vol 1, A171-L
Ref: Daniel (1902), 297

Nitramidon. Fr for Nitrostarch

Nitramin. Another name for Tetryl

Nitramidine. Expl compd prepd in 1845 by Dumas by the nitration of paper or cardboard, and proposed for use in the manuf of cannon cartridges (gargousses in Fr). This material was prepd prior to the discovery of NC by Schönbein
Ref: Daniel (1902), 453

Nitramines. See under Amines, Nitratred and Nitritred in Vol 1, A174-R to A177-R, and Amine, Catalyzed Nitration in Vol 1, A174-L
Addnl Refs: 1) R.J.J. Simkins, M.A. Simpkins & G.F. Wright, “Nitramine Abstracts”, 4 Vols, Univ of Toronto (1953) [An unclassified collection of paper and patent abstracts on the chemistry of nitramines and their isomers, including primary nitramines, their N- and O-alkyl derivs, permitsoso compds, nitrimines, and nitrosohydroxylamines and their ethers]
2) Urbasński 3 (1967), 15–127 [aliphatic, aromatic and heterocyclic nitramines]

Nitraminoalcohols. See under Aminoalcohols, Nitratred and Nitritred in Vol 1, A179-L to A180-L

Nitraminobenzenes. See under Aminobenzenes and Derivatives in Vol 1, A185-L

Nitraminoethane, N-Nitroethylamine or Ethyl-nitramine. See in Vol 1, A199-R

1-Nitramine-2-ethanol Nitrate, N-(β-Nitroxy-ethyl) nitramine or NENA. See in Vol 1, A201-L

Nitrarninoimidazoles, Nitrarninoimidazolidines, Nitrarninoimidazolines.
See under Aminoimidazoles in Vol 1, A218-R, etc

Nitrarninopropanol Nitrate, 1-Nitrarnino-2-nitroxypropane or IsoMeNENA. See under Aminopropanols and Derivatives in Vol 1, A253

6-Nitrarnino-s-triazone-2,4-diol. See under Ammelide and Derivatives in Vol 1, A273

5-Nitrarninotetrazole of Lieber and Its Salts.
See in Vol 1, A260-L

5-Nitrarninotetrazole of O’Connor and Its Disodium Salt. See in Vol 1, A259-R

Nitramita de la Fábrica de Galdácano (Spanish).
See under Coal Mining Explosives, Permissible in Vol 3, C455-L

Nitramita Española de la Fábrica de Granada (Spanish). See under Coal Mining Explosives, Non-Permissible in Vol 3, C442-L

Nitramite. Trademark for a series of nitrocarbonate blasting agents developed by the duPont Co. Nitramite 2 was developed to provide a lower cost supplemental charge in columns of Dynamite for large diameter boreholes. It has become a popular blasting agent, and is frequently used for column loads where column build-up or a moderate degree of w resistance is required. Its d ranges from 1.07 to 1.14g/cc, it will sink in w, and is frequently used as a bottom load in wet holes. Nitramite 2 provides excellent performance for top loading in quarries and open pits, and is well adapted for stripping operations in both vertical and horizontal holes (Refs 2, 3 & 4)
The name Nitramite was also applied to a group of expls proposed by P. deWilde and patented by the Société Suisse d’Explosifs. Nitramite No 1 was prep'd by passing the gas obtained during the catalytic dehydrogenation of ammonia-methanol thru nitric acid. Its compn was AN 70–80% and a mixt of the nitrates of mono-, di- and trimethylamines 30–20%. Its properties, as detd in 1935–36 at the Laboratoire Central des Poudre were as follows: mp ca 120°, bp ca 230°; hygroscopic; sensitivity to shock: 50% expls with 10kg wt dropping 2.50m, difficult to inflame; gap test: 1 cm between 50g cartridges at d 1.20g/cc; French Trauzl test (c.u.p.) 115 (PA 100); vel of deton (max) 3200m/sec at d 1.20 to 1.30g/cc.

Nitramite No 2 contd AN 70–80 & methylam- nite 30–20%. Vel of deton (max) 3250m/sec at d 1.25/cc (Ref 1)

See also under Italian Ammoniums in Vol 1, A291-R, Italian Explosives in Vol 7 & Spanish Explosives


Nitramon. Trademark for a series of nitrocarbonate blasting agents developed by the duPont Co. They cannot be detonated by the strongest commercial blasting caps, a line of detonating cord, flame, shock, friction, or the impact of ball ammo or of heavy steel wts. Their blasting energy is released by the use of “Nitramon” primers, also manufd by DuPont. Nitramon has given outstanding results in the quarrying of almost every type of material, including limestone, sandstone, granite, trap rock, cement rock and shale. It is also used in stripping the overburden from both hard and soft coal, and in open pit mines for ore blasting as well as stripping.

There are several grades of Nitramon, including A and HH, as well as S and S-EL, intended for seismic prospecting, and WW and WW-EL, for use in seismic prospecting at sea.

Nitramon A has the highest d (1.27 to 1.48 g/cc) and is comparable in performance to 60% Special Gelatin.

In anthracite coal strip fields, it becomes necessary at times to blast burning rock formations overlying the coal. In the removal of burning mine refuse banks, fused material that requires drilling and blasting is often encountered. Some of this may have temps above normal due to continued burning. As a result, temps of several hundred degrees are encountered in large diameter drill holes. The use of Dynamite under such conditions becomes extremely hazardous, and Nitramon HH was developed to meet this need.

Nitramon S possesses strength and vel of the same magnitude as the gelatin Dynamites normally employed in seismic-prospecting. Actual field tests have demonstrated that comparable seismograph records are obtained when a given wt of 60% gelatin is replaced by a column of Nitramon S and a primer of equal wt and length. Nitramon S-EL provides approx 65% greater useful seismic energy return than does Nitramon S.

Nitramon WW has a d of approx 1.2g/cc, which allows it to sink readily in w, but at the same time does not require an excessive amt of buoyant material for suspended charges. Nitramon WW-EL returns about 65% greater useful seismic energy than Nitramon WW.

Ref: Blaster’s Hndbk (1969), 47–55

Nitramonita. Expl manufd by La Dinamita Nobel Italiana contg RDX 80 & MNN 20%

Ref: Vivas, Feigenspan & Ladreda 2 (1946), 288

Nitranilic Acid. See 3,6-Dinitro-2,5-dihydroxy-1,4-benzaquinone in Vol 5, D1290-L

Nitrasols. Family of castable composite solid propants contg plastisol binders composed of plastisol NC and certain liq nitrate esters. The liq esters serve as a plasticizer for the NC, yielding an elastomeric binder of very high energy.

The work that led to the development of Nitrasol propants began at the US Naval Ordn Test Station (NOTS) in 1955 with a program of research on elastomeric propants, in which the aim was to tie the plasticizer chemically to the NC to prevent migration of the plasticizer to the inhibitor. In attempting to solve processing problems met in the formulations under investi-
gation, NOTS took advantage of work done on plastisol NC by the Atlantic Research Corp, which had been the first to prepare this material and use it in propellants. NOTS modified an Atlantic Research Corp procedure and began to prepare plastisol NC to meet its own specifications. At the same time that NOTS began producing its own plastisol NC, binder studies showed that a 40/40/20 mixt of Pentaerythritol Trinitrate (Petrin), NC, and dibutyl phthalate held considerable promise as an elastomeric propellant binder. Later, binders were developed contg only the high-energy nitrate esters Petrin and Trimethylolmethane Tri-

nitrate (TMETN), with no dibutyl phthalate

The following table shows the formulation, physical and ballistic properties of two Nitrosol propellants with widely differing applications. The H3515 formulation is a high energy propellant, while P3500 is an application to gas-generator propellants.

Table 1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Propellant formulation, % composition</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>High Energy, H3515</td>
</tr>
<tr>
<td>Plastisol nitrocellulose (12.6% N)</td>
<td>14.25</td>
</tr>
<tr>
<td>Pentaerythritol trinitrate</td>
<td>35.00</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>-</td>
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<tr>
<td>Ethyl centralite</td>
<td>0.75</td>
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<tr>
<td>N-methyl-p-nitroaniline</td>
<td>-</td>
</tr>
<tr>
<td>2-Nitrodiphenylamine</td>
<td>-</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>-</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>-</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>-</td>
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<tr>
<td>Ammonium perchlorate</td>
<td>35.00</td>
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<tr>
<td>Aluminum</td>
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Tensile strength at 77°F, psi

<table>
<thead>
<tr>
<th></th>
<th>High Energy, H3515</th>
<th>Gas generator, P3500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>164</td>
<td>270</td>
</tr>
<tr>
<td>At rupture</td>
<td>164</td>
<td>201</td>
</tr>
<tr>
<td>Elongation at 77°F, %</td>
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<td></td>
</tr>
<tr>
<td>At maximum tensile strength</td>
<td>124.6</td>
<td>12.2</td>
</tr>
<tr>
<td>At rupture</td>
<td>124.6</td>
<td>23.2</td>
</tr>
<tr>
<td>Modulus of elasticity at 77°F,</td>
<td></td>
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</tr>
<tr>
<td>psi x 10^3</td>
<td>0.78</td>
<td>5.26</td>
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<tr>
<td>Density, lb/cu inch</td>
<td>0.064</td>
<td>0.0602</td>
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<tr>
<td>Impact sensitivity of ground propellant,</td>
<td>8</td>
<td>170</td>
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<tr>
<td>50% point with 2-kg hammer, cm</td>
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<tr>
<td>Friction sensitivity, kg-cm</td>
<td>56</td>
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<tr>
<td>Electrostatic sensitivity, joules</td>
<td>41.6</td>
<td>-</td>
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<td>Strand burning rate at 70°F</td>
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</tr>
<tr>
<td>and 1000 psi, in/sec</td>
<td>0.42</td>
<td>0.48</td>
</tr>
<tr>
<td>Pressure exponent</td>
<td>0.68</td>
<td>0.79</td>
</tr>
<tr>
<td>Temperature coefficient (mp/r),</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%/°F</td>
<td>0.22</td>
<td>1.97</td>
</tr>
<tr>
<td>Specific impulse (isp),</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lbf-sec/lbm</td>
<td>255\textsuperscript{a}</td>
<td>156\textsuperscript{b}</td>
</tr>
<tr>
<td>Adiabatic flame temperature, 0^\circ K</td>
<td>3450</td>
<td>955</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Measured value corrected to 1000 psi.

\textsuperscript{b}Calculated
The P3500 contains AN as the solid oxidizer. Since the Nitrasol binder was used in this propellant, only 35% AN was required to obtain a relatively clean and cool-burning propellant. Comparable propellants require 70% or more solid oxidizer to achieve the same burning properties. P3500 is thus relatively immune to the two major problems, phase changes and hygroscopocity, that exist with propellants containing large proportions of AN.

The physical properties of Nitrasol make it applicable to the motors of very large missiles. Cracking under the stresses of ignition is eliminated, because Nitrasol has an elongation two to three times that of other composite propellants now in use. In case-bonded rocket motors this property prevents cracking from temp changes. Nitrasol has a relatively high tensile strength, and can be easily cast into well-defined shapes, making it particularly well-suited for the fabrication of grains of intricate design.

Nitrasol can be mixed in standard equipment, with precautions to exclude moisture not being necessary. It is cast without vacuum in the mold or press in the mixer. Since neither the mixing nor the curing involves any chemical reactions, there are no exotherms. In mixing Nitrasol, the liq ingredients are weighed and thoroughly mixed. The plastisol NC is placed in a sigma-blade or similar type of mixer, and approx 40% of the liquids are added. These ingredients are mixed until the plastisol NC agglomerates have been broken up and all the particles have been wetted; this requires approx 15 minutes. The remainder of the liq ingredients are added, and mixing is continued for 30 minutes under vacuum. The AI is added and mixing is resumed until all the AI has been wetted. The AP is added and the mixing and degassing are again resumed for 30 minutes. During the last 15 minutes of the mixing period, warm water is run thru the mixer jacket to raise the temp of the finished propellant mix to 110°F. The propellant is then poured directly from the mixing vessel into the casting mold without the aid of press or vacuum. The propellant is presently cured by maintaining it at a temp of 185°F max for from one to two hours (Ref 1).

Electrical vol resistivity techniques have been employed to follow the course of the hardening of Nitrasol expls (Ref 3). The air blast effectiveness of Nitrasol as a high expl indicated it is a better expl than Pentoilite and a poorer one than H-6 (Ref 2), and its use as an underwater expl has been investigated (Ref 4).


LIST OF NITRATE COMPOUNDS

Ammonium Nitrate. See in Vol 1, A311 to A340

Barium Nitrate. See in Vol 2, B20-R to B21-I

Calcium Nitrate (Lime Nitrate, Nitrocalcite, Lime Saltpeter, Norwegian Saltpeter). (a) Ca(NO₃)₂, mw 164.10, N 17.07%, OB to CaO & N₂ +48.8%, deliq granules, mp 561°F, d 2.36g/cc. Can be prepd by neutralizing lime with nitric acid. Sol in w (102p at 0°F, 376p at 151°F), in alc (14p at 15°F) and amyl alc. (b) Ca(NO₃)₂.4H₂O, mw 236.1, white deliq mass, mp 42°F, d 2.36g/cc, v sol in w. Strong oxidizing agent and dangerous fire risk in contact with organic materials; may expl if shocked or heated. Used in expls, pyrots, matches & fertilizers (Refs 6, 7 & 8)

Na₂O₃ (Ref3 & 5) patented blasting expls made by dehydrating Ca nitrate at temps above 100°F, cooling and grinding it, followed by mixing with TNT, NG, charcoal & sawdust. The Ca nitrate content varied from 62-70%. Stoops (Ref 2) patented expls contg hydrated Ca nitrate mixed with AN & K nitrate in Amm perchlorate, and absorbed on sawdust. Haid et al (Ref 4) claimed that a Ca nitrate mixt dried at 120°F was superior to a saltpete blasting powder.

There is no US Specification for Ca nitrate.
Cellulose Nitrato. See in Vol 2, C100-L to C126-L.

Cellulose Benzoate Nitrates. See in Vol 2, C99-L.

Ceric Ammonium Nitrate (Cerium Ammonium Nitrate, Ammonium Hexanitratocerate). Ce(NO₃)₄·2NH₄NO₃, mw 548.3, small prismatic yellow crystals, soln in w & alc. Prepd by electrolytic oxidation of cerous nitrate in nitric acid soln, and subsequently mixing solns of cerium nitrate and AN, followed by cryst. In a strong oxidizing agent and a dangerous fire risk in contact with organic materials.

In the expts laboratory it is used for the detn of Pb Azide (LA) in primer mixts. The reaction proceeds as follows (Ref 2):

\[ \text{PbN}_4 + \text{Ce(NO}_3)_4 + 2\text{NH}_4\text{NO}_3 \rightarrow 3\text{N}_2 + \text{Pb(NO}_3)_2 + 2\text{Ce(NO}_3)_3 + 4\text{NH}_4\text{NO}_3 \]

with the quant production of nitrogen gas which is collected in an azometer (measuring tube) and used for the detn of the azide radical (see Vol 1, A566-L). It can also be used for the destruction of LA or other azides. There is no US Specification for Ceric Ammonium Nitrate.


Ethyl Nitrato. See Vol 6, E143-R

Litharge in hot dil nitric acid of d 1.35g/cc, and partially evap the soln.

It is a strong oxidizing agent, highly toxic, and a dangerous fire risk in contact with organic materials.

Pb nitrate is used in matches, in some military expls (Macaire, Triplastite, etc), and in the manuf of LST & LA. According to Taylor & Rinenbach (Ref 1), the use of Pb nitrate in the manuf of expls has been minimal mainly because of its tendency to decompose on slight heating or in contact with other chemicals. This disadvantage offsets the advantages of being less hygroscopic than other nitrates, except for K nitrate, and of contg more oxygen per unit vol than any other common oxidizing substance. As it gives off poisonous fumes on expl, its use in composite expls has been prohibited in Engl.

US Mil Spec MIL-L-20549A, “Lead Nitrato, Technical” (15 Jan 1968) contains the following requirements: Pb nitrate shall be white in color and conform to these chemical characteristics: Assay as Pb(NO₃)₂, 98.0% min; w content, 1.25% max; w-insol matter, 0.20% max; acidity (as HNO₃), 0.50% max; Cu, 0.002% max.


Lithium Nitrato. LiNO₃, mw 68.95, N 20.32%, colorless deliq granules, mp 261°C, d 2.38g/cc, soln in w & alc. Prepd by reaction of nitric acid with Li carbonate. It is a strong oxidizing agent and a dangerous expln risk when shocked or heated. It is used in pyrots as an oxidizer to color burning compns red. There is no US Specification for Li nitrate.


Magnesium Nitrato. Mg(NO₃)₂·6H₂O, mw 256.43, N 10.93%, OB to MgO & N₂ +68.6%, colorless deliq crysts, mp 95°C, d 1.464g/cc, loses 5H₂O at 330°C. Soln in 8p w, freely soln in alc. Prepd by the action of nitric acid on Mg oxide with subsequent
potassium nitrate (salt peter, nitre, sal prunella, niter). kno₃, mw 101.10, n 13.86%, ob to k₂o & n₂ +39.6%, colorless prismatic or rhombohedral crystals, d 2.1062 to 2.109g/cc, mp 333°c, bp, decomps at 400° with evolution of o₂ and deslagination, r1 1.5038 for rhombohedral crystals (refs 9, 12 & 13)

k nitrate was first obtained, in admixture with na nitrate, by boyle in 1667. the oldest method of prep, which is still used in india and egypt, is in the so-called "nitre plantations". such plantations are usually located near towns or villages, where urine and other organic material find their way into the calcareous soil, owing to imperfect systems of sewage disposal. due to the action of microorganisms on urea, etc, some ammonia, which is first formed, is oxidized to nitric acid and this, reacting with ca carbonate of the soil, forms ca nitrate. this material is leached with w and the resulting soln is boiled with wood ashes, which contain k carbonate:

ca(no₃)₂ + k₂co₃ → cao₃ + 2kno₃

the filtrate on evap deposits salt peter, which is purified by crystn.

salt peter may also be obtained from specially constructed "heaps" of nitrous earth from which it is leached with w. this method is still in use in india (ref 1, p 57)

production as practiced in chile consists of leaching residues from their na nitrate operation to produce a weak brine of k nitrate which is coned by solar evap. when the proper concn of k nitrate is achieved it is recovered by crystn (ref 14)

a process for production of k nitrate from k chloride and nitric acid, after several years of development, was placed in commercial production in the usa in 1963. the overall process is represented by the following equation:

2kcl + 2hno₃ + ½o₂ → 2kno₃ + cl₂ + h₂o

it is rather complicated and details cannot be given here, but the key to its success is the oxidation of nitratesyl chloride according to the reaction:

nocl + 2hno₃ → 3no₂ + ½cl₂ + h₂o

the nitrogen dioxide product is converted to nitric acid for recycle in the process. the process has been described in detail by spealman (ref 11)
Solubility (Ref 3)

Water (grams K nitrate per 100g w)

<table>
<thead>
<tr>
<th>°C</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>13.43</td>
</tr>
<tr>
<td>14.90</td>
<td>25.78</td>
</tr>
<tr>
<td>25</td>
<td>38.45</td>
</tr>
<tr>
<td>30.80</td>
<td>47.52</td>
</tr>
<tr>
<td>44.75</td>
<td>74.50</td>
</tr>
<tr>
<td>60.05</td>
<td>111.18</td>
</tr>
<tr>
<td>76</td>
<td>156.61</td>
</tr>
<tr>
<td>91.65</td>
<td>210.20</td>
</tr>
<tr>
<td>114 (bp)</td>
<td>311.64</td>
</tr>
</tbody>
</table>

Abs Methanol. Practically insol

Aq Methanol (grams per 100g of satd soln at 30°)

<table>
<thead>
<tr>
<th>Grams CH₃OH</th>
<th>Grams KNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.3</td>
</tr>
<tr>
<td>7.8</td>
<td>23.3</td>
</tr>
<tr>
<td>17.3</td>
<td>16.3</td>
</tr>
<tr>
<td>27.8</td>
<td>11.2</td>
</tr>
<tr>
<td>38.4</td>
<td>7.7</td>
</tr>
<tr>
<td>57</td>
<td>3.8</td>
</tr>
<tr>
<td>98.58</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Absolute Ethanol. Practically insol

Aq Ethanol (Grams per 100g of satd soln at 30°)

<table>
<thead>
<tr>
<th>Grams C₂H₅OH</th>
<th>Grams KNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>20.7</td>
</tr>
<tr>
<td>23.8</td>
<td>12.1</td>
</tr>
<tr>
<td>32.2</td>
<td>9.0</td>
</tr>
<tr>
<td>43.1</td>
<td>6.1</td>
</tr>
<tr>
<td>56.9</td>
<td>3.3</td>
</tr>
<tr>
<td>76.8</td>
<td>0.88</td>
</tr>
<tr>
<td>92.3</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Ether. Practically insol

Trichloroethylene. 0.01g K nitrate per 100g solvent at 15°

Hydrazine (anhyd). 14g K nitrate per 100ml solvent at RT

Liq Ammonia. 100g of satd soln contains 9.52g K nitrate and 10.52g NH₃ at 0°; 9.42g and 10.4g, respectively, at 25°

Hygroscopicity (Ref 6)
The weight gain of K nitrate in mgs/g at RT after equilibrium was established in vacuum desiccators is shown below:

<table>
<thead>
<tr>
<th>% Rel Humidity</th>
<th>65</th>
<th>75</th>
<th>86</th>
<th>93</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time 24hrs equil</td>
<td>24hrs equil</td>
<td>24hrs equil</td>
<td>24hrs equil</td>
<td>24hrs equil</td>
</tr>
<tr>
<td>Specification Grade</td>
<td>–</td>
<td>&lt;1</td>
<td>–</td>
<td>0.2</td>
</tr>
<tr>
<td>Purified Material</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

The critical relative humidity of Specification grade K nitrate is 91.7% at 20°; purified material, 91.8% at 26.2°

Moisture absorbed by 2.0g of CP K nitrate at 25° as a function of fineness is shown below:

<table>
<thead>
<tr>
<th>Finess</th>
<th>Exposure</th>
<th>H₂O Absorbed, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>40–80 mesh</td>
<td>2.75</td>
<td>0.0147</td>
</tr>
<tr>
<td>18.75</td>
<td>0.1136</td>
<td></td>
</tr>
<tr>
<td>25.25</td>
<td>0.1527</td>
<td></td>
</tr>
<tr>
<td>42.75</td>
<td>0.2687</td>
<td></td>
</tr>
<tr>
<td>47.00</td>
<td>0.2896</td>
<td></td>
</tr>
<tr>
<td>Ground Very Fine</td>
<td>7.25</td>
<td>0.0453</td>
</tr>
<tr>
<td>16.50</td>
<td>0.1056</td>
<td></td>
</tr>
<tr>
<td>40.50</td>
<td>0.2580</td>
<td></td>
</tr>
</tbody>
</table>

Specification grade K nitrate gains 0.76% by wt at 70°F and 90% relative humidity

Toxicity. Ingestion of large amounts may cause violent irritation of the intestinal lining. Prolonged exposure to small amounts may result in anemia and nephritis. Moderately poisonous on ingestion or inhalation (Refs 9 & 10)

Fire and Explosion Hazard. Dangerous, as K nitrate is both a fire and explhn hazard. As a strong oxidizer it can give up its oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decomp. It is sensitive to shock, can be very easily detonated, and when mixed with flammable materials becomes very sensitive (Refs 6 & 10)

Properties: The products of decomp, from 650 to 750°, are KNO₂+O+traces of NO₂. At 800° decomp is more extensive with KNO₂ decomposing to form K₂O, N and O (Ref 5). For DTA and TGA data, see Ref 4

When dried and powdered K nitrate is thrown on red-hot charcoal, or when powdered charcoal is sprinkled on fused K nitrate, rapid combustion occurs, possibly:

4KNO₃+5C → 2K₂CO₃+3CO₂+2N₂, so that 1
vol of solid K nitrate will give on decompo
nearly 3000 times its vol of gas (Ref 2). It is
this fact that makes K nitrate so valuable an
ingredient of BlkPdr and other expl mixts
Uses: K nitrate is used in the manuf of BlkPdrs,
time fuzes, matches, and blasting expls, with or
without NG. In proplnts, it is employed as an
additive to avoid or diminish flash, and to make
the proplnt more ignitable (Ref 7). Aside from
use in BlkPdr and some starter mixts, its main
pyrotechnic application is as the oxidizer in
B/K nitrate ignition pellets (Ref 8)
The US Dept of Defense Mil Spec for K
nitrate is MIL-P-156B (18 April 1956) with
Amendment 1 (31 July 1974). Three classes
are specified: Class 1 — for use in black powder
and chemical munitions; Class 2 — for use in
pyrotechnic compositions; and Class 3 — for
use in propellants. The chemical requirements
for these classes are given below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Class 1</th>
<th>Class 2</th>
<th>Class 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture, max</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>pH value</td>
<td>7 ± 1</td>
<td>7 ± 1</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>Water insol material, max</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Grit</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Chlorides, as KCl, max</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Chlorates &amp; perchlorates, as KClO₄, max</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Iron &amp; aluminum, as oxides, max</td>
<td>0.5</td>
<td>0.5</td>
<td>—</td>
</tr>
<tr>
<td>Calcium &amp; magnesium, as oxides, max</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium, as oxides, max</td>
<td>0.25</td>
<td>0.25</td>
<td>—</td>
</tr>
<tr>
<td>Ammonium compounds</td>
<td>None</td>
<td>None</td>
<td>—</td>
</tr>
<tr>
<td>Nitrogen, min</td>
<td>13.77</td>
<td>13.77</td>
<td>13.77</td>
</tr>
</tbody>
</table>

The potassium nitrate shall be odorless, and
the crystals white in color
Granulation requirements specify that Class
1 material shall be furnished in lump form,
while Class 2 and 3 material shall comply with
the following, using US Standard sieves:

<table>
<thead>
<tr>
<th>Sieve No</th>
<th>Percent, min, thru specified sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 2</td>
</tr>
<tr>
<td>60</td>
<td>99.9</td>
</tr>
<tr>
<td>80</td>
<td>—</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
</tr>
</tbody>
</table>

Refs: 1) Marshall 1 (1917) 53–66; 2 (1917),
717–18; 3 (1932), 9–11 2) Mellor 2 (1922),
809 & 820 3) Seidell 1 (1940), 833–50
4) S. Gordon & C. Campbell, AnalChem 27,
1102 (1955) 5) E.S. Freeman, JACS 79,
838 (1957) 6) Anon, EngrDesHndbk,
"Military Pyrotechnics Series, Part Three—
Properties of Materials Used in Pyrotechnic
Compositions", AMCP 706-187 (1963), 247
7) Anon, EngrDesHndbk, "Solid Propellants,
Part 1", AMCP 706-175 (1964), 50 8) Ellern
(1968), 339 9) Merck (1968), 855R
10) Sax (1968), 246–8 11) I. Spealman,
"Farm Chemicals Handbook", Meister Publ Co
723-R 13) Hackh's (1972), 540-R
14) J.A. Kent, Ed, "Riegel's Handbook of In-
dustrial Chemistry", 7th Ed, VanNostrand

Propyl Nitrates. See under Propane

Sodium Nitrate (Chile Saltpeter, Cubic or Soda
Niter, Caliche, Nitratine). NaN₃, mw 85.01,
N 16.48%, OB to Na₂O and N₂ +47%; colorless,
transparent crystals, white granules or powd; mp
308°; bp, dec at 380°, explodes at 1000°F,
d 2.267g/cc, RI 1.5874. One g dissolves in
1.1ml w, 0.6ml boiling w, 125ml alc, 52ml
boiling alc, 3470ml abs alc, 300ml abs methanol
(Refs 5 & 7)
Na nitrate occurs native in large deposits in
the rainless districts of Chile, hence it is often
called "Chile saltpeter" or "Chile niter". The
Na nitrate in the deposits constitutes from 20
to 50% in a distinct stratum of earth known as
"caliche". The caliche is crushed and lixiviated
in large tanks of w heated by steam. The settled
soln is run off to crystallizers, where crude
nitrate separates, the mother liquors being run
back to the lixiviators. The crystals are washed
with a little w and dried in the sun; they con-
tain 95–96% Na nitrate (Ref 1)

In the early days of fixation of atmospheric
N₂, when the arc process was used in Norway
to produce NO from air, the effluent from the
arc furnaces was cooled to about 50°, the NO
was oxidized by the same air to NO₂, and the
NO₂ was absorbed in an aq soln of soda ash
which reacted with NO₂ to form both Na nitrate and nitrite in the soln:
\[ \text{Na}_2\text{CO}_3 + 2\text{NO}_2 \rightarrow \text{NaNO}_3 + \text{NaNO}_2 + \text{CO}_2 \]
Then air was blown thru the soln to oxidize the Na nitrate to nitrate after which the soln was coned by evapn, and Na nitrate was recovered by crystallization.

Later, when nitric acid was manuf'd from synthetic ammonia at relatively low cost, synthetic sodium nitrate was made from it either thru the reaction between nitric acid and soda ash, or by direct absorption of nitrogen dioxide in an aq soln of Na carbonate (see above equation). The Na nitrate-nitrite soln was then heated with excess nitric acid to convert the nitrite to nitrate, and the NO thus produced was recycled to the nitric acid plant (Ref 6).

\[ Q_{\text{f}}^{298^\circ} = -111540 \text{cal/mole}; \text{ specific heat, } 0.262 \text{cal/g at } 25^\circ; \text{ latent heat of fusion is } -5355 \text{cal/mole at } 310^\circ \] (Ref 6)

**Hygroscopicity** (Ref 3): Na nitrate deliquesces in moist air. The critical relative humidity of purified material is 82.7% at 20°. The wt gain of purified Na nitrate (41 μ size) at 70° after 120 hours exposure is 11% at 70% RH and 25.7% at 90% RH. Water absorbed by 2.000g of 40–80 mesh material at 25° is:

<table>
<thead>
<tr>
<th>Hours</th>
<th>g H₂O absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.0713</td>
</tr>
<tr>
<td>5.5</td>
<td>0.1355</td>
</tr>
<tr>
<td>7.5</td>
<td>0.1970</td>
</tr>
<tr>
<td>16</td>
<td>0.3924</td>
</tr>
</tbody>
</table>

**Fire and Explosion Hazard.** Na nitrate is a dangerous fire and expl. hazard. It can ignite on friction. When heated above 1000° or when heated with reducing materials, particularly cyanides, it emits toxic fumes on decomp (Ref 3).

**Properties.** When molten Na nitrate is heated, it begins to decomp at 380°. At 400–600°, it gives off N₂ and O₂. NO appears at 700°. The rate of decomp increases with temp. From 775 to 865°, small amts of NO₂ and N₂O are also formed. The residue of the decomp is Na₂O. For DTA & TGA data see Ref 2.

**Uses.** Na nitrate is an oxidizing agent containing more available oxygen per unit wt than K nitrate, and for this reason it is a suitable ingredient of expls such as black blasting powders (introduced by duPont) and some Dynamites (see Vol 5, D1584ff). A more extensive use of it could be made if it were not so hygroscopic. In pyrotechnics, the oxidizer of choice for high-energy white flares is Na nitrate. It fulfills several important functions: the reaction with Mg leads to the formation of white Mg oxide particulates which enhance light reflection; the heat of reaction per g of components is high because of the high oxygen content of the nitrate and the low equivalent wt of the Na; and the Na exhibits luminescent properties that add significantly to useful light production (Ref 4).

The US Dept of Defense Mil Spec for Na nitrate is MIL-S-322C (5 Feb 1968). Three grades are specified (A, B & C) based on chemical requirements, and three classes (1, 2 & 3) based on granulation requirements. The chemical requirements are given on the following page.

In addition to the granulation requirement, the average particle diameter of Class 2 Na nitrate shall be 30±15 microns by the procedure specified in MIL-STD-1233, Method 100.

**Refs:**
1) Partington (1950), 694  2) S. Gordon & C. Campbell, AnalChem 27, 1102 (1955)
Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Grade A Percentage</th>
<th>Grade B Average Percentage</th>
<th>Grade C Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Max: 0.75</td>
<td>Min: –</td>
<td>Max: 0.5</td>
</tr>
<tr>
<td>Insoluble Matter</td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Alkalinity (as Na₂O)</td>
<td>0.05</td>
<td>None</td>
<td>0.1</td>
</tr>
<tr>
<td>Nitrates (as NaNO₃)</td>
<td>97.0</td>
<td></td>
<td>99.5</td>
</tr>
<tr>
<td>Chlorates (as KClO₃)</td>
<td>0.06</td>
<td>None</td>
<td>0.1</td>
</tr>
<tr>
<td>Calcium (as CaO)</td>
<td>0.3</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>Magnesium (as MgO)</td>
<td>0.15</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>Sulfates (as Na₂SO₄)</td>
<td>0.5</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>Chlorides (as NaCl)</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
</tbody>
</table>

1/ The percentages indicated, except the percent of moisture, are to be obtained in the sodium nitrate after the sample has been dried to constant weight at 150 ± 3°.

Granulation requirements follow:

Table 2

<table>
<thead>
<tr>
<th>US Standard Sieve Number</th>
<th>Class 1 Percent thru</th>
<th>Class 2 Percent thru</th>
<th>Class 3 Percent retained on</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>Minimum</td>
<td>Minimum</td>
<td>Minimum</td>
</tr>
<tr>
<td>20</td>
<td>–</td>
<td>–</td>
<td>80.0</td>
</tr>
<tr>
<td>60</td>
<td>98.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>100</td>
<td>–</td>
<td>98.0</td>
<td>–</td>
</tr>
<tr>
<td>200</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>325</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Strontium Nitrate.** Sr(NO₃)₂, mw 211.65, N 13.24%, OB to SrO and N₂ +37.8%, white granules or powd, mp 570°; bp decomp 580–600°; d 2.99g/cc, RI 1.5878. A white monoclinic tetrahedrate, Sr(NO₃)₂.4H₂O, also exists, having a d of 2.2g/cc. Methods reported for making Sr nitrate are by (1) treating strontianite with nitric acid, (2) digesting celestite with soda ash followed by treatment with nitric acid, and (3) digesting celestite with coal in a rotary kiln to form a sol sulfide, followed by treatment with nitric acid. Sr nitrate solns so formed are purified, and a commercial Sr nitrate crystal of high purity is prepbd by crystn. Sol in 1.5p w, al sol in alc or acet (Refs 3, 5 & 6).

**Hygroscopicity.** The critical relative humidity of purified Sr nitrate is 82.7% at 20°; for Spec grade material, 82.9% at 26.2° (Ref 2).

**Fire and Explosion Hazard.** Sr nitrate is a fire and expln hazard. As an oxidizer it can give up oxygen to other materials to produce a vigorous reaction which may result in detonation. Toxic fumes are emitted on decompn. May expld when shocked or heated (Refs 2 & 6). For DTA or TGA data see Ref 1.

**Uses.** The main use for Sr nitrate is for producing red colors in pyrotechnics, railroad fuses, marine signals, tracer compositions and in matches (Refs 2, 4 & 7). A high degree of purity is required, for the contamination of Sr nitrate with
Na or Ca salts tends to lighten the scarlet red flame to reddish yellow (Ref 5).

The US Dept of Defense Spec for Sr nitrate is MIL-S-20322B (19 Apr 1973). Two grades are specified, Grade A for use in pyrotechnic compns, such as flares, and Grade B, for use in tracer compns. The chemical and physical requirements are given below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium nitrate (including any barium nitrate), %, min</td>
<td>99.5 99.5</td>
</tr>
<tr>
<td>Moisture, %, max</td>
<td>0.05 0.05</td>
</tr>
<tr>
<td>Hygroscopicity, %, max</td>
<td>0.05 0.05</td>
</tr>
<tr>
<td>Acidity (pH)</td>
<td>6.0–7.0 6.0–7.0</td>
</tr>
<tr>
<td>Water-insoluble matter, %, max</td>
<td>0.02 0.02</td>
</tr>
<tr>
<td>Grit, %, max</td>
<td>0.02 0.02</td>
</tr>
<tr>
<td>Chloride (as Cl), %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Ammonium compounds (as NH₃), %, max</td>
<td>0.01 0.01</td>
</tr>
<tr>
<td>Sulfur (total), %, max</td>
<td>0.01 0.01</td>
</tr>
<tr>
<td>Barium, %, max</td>
<td>0.05 1.5</td>
</tr>
<tr>
<td>Calcium, %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Magnesium, %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Sodium, %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Iron, %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Bismuth, %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Lead, %, max</td>
<td>0.003 0.003</td>
</tr>
<tr>
<td>Copper, %, max</td>
<td>0.003 0.003</td>
</tr>
</tbody>
</table>

The granulation requirements for Grade A material is 95% thru a US Standard No 100 sieve; for Grade B material, 99.9% min thru a US Standard No 50 sieve, and 70.0% min retained on a US Standard No 140 sieve.


Tin Nitrate. Stannic nitrate, Sn(NO₃)₄, has been reported, but its existence is questionable. A soln contg stannic tin (Sn⁴⁺) can be made by dissolving Sn in nitric acid. It decomp on aging, heating or dilution. The existence of stannous nitrate, Sn(NO₃)₂, must also be questioned. A soln of stannous tin (Sn²⁺) in nitric acid can be made which must be kept cold. It is unstable to heat, dilution and aging (Ref 3).

In view of the above modern ref, it is interesting to note that Daniel (Ref 1) reported that tin nitrate (Nitrate d'étain in Fr) could be prepd by pouring a thin layer of nitric acid (d 1.2g/cc) onto a Sn surface and allowing it to stand for a while. A soln of Cu nitrate could be used in lieu of nitric acid. The resulting grayish-white deposit could be gently scraped with a non-sparking metal blade and dried. After drying, the material proved to be extremely sensitive to heat, impact or friction (Ref 1).

The above Sn nitrate (?) deserves mention because it was thought to be a fire and expln hazard in industrial accidents. For example, at the Spandau plant in Ger, several fires erupted in areas where wet NC came in constant contact with soldered bronze joints. In order to prevent further incidents, all soldered joints were examined and were found to be corroded with a coating contg Sn and nitrate ions. It was also found that the corroded material exploded when removal with a chisel was attempted.

Ellern (Ref 2) mentions that in the presence of w, cupric nitrate and Sn foil, on prolonged and intimate contact, will produce flaming and sparking.


Uranyl Nitrate (Uranium Nitrate, UNH, Yellow Salt). UO₂(NO₃)₂·6H₂O, mw 502.18, N 5.58%; yellow rhomb crystals, greenish luster by reflected light; mp 60.2°, bp 118°, d 2.807g/cc, RI 1.4967. Sol in 1.5p w, freely in alc and eth. Prepd by the action of nitric acid on U octoxide. When shaken, rubbed, or crushed, the crystals show remarkable triboluminescence with occasional detonations. It is highly toxic, and a severe fire and expln risk when shocked or heated.
and in contact with organic materials. Solns of U nitrate in eth should not be allowed to stand in sunlight as expln may occur.


Zinc Nitrate. Zn(NO₃)₂·6H₂O, mw 297.49, colorless tetragonal crs, mp 36.4°, loses 6H₂O from 105° to 131°, d 2.065g/cc. Sol in w and alc. Prepd by action of nitric acid on Zn or Zn oxide. It is a strong oxidizing agent, a dangerous fire and expln risk, and may expld if shocked or heated.

The US Dept of Defense Spec for Zinc Nitrate, Reagent is MIL-Z-11143 (10 May 1951), and specifies the following chemical requirements:

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay, as Zn(NO₃)₂·6H₂O</td>
<td>99.0 minimum</td>
</tr>
</tbody>
</table>

**Table 1**

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay, as Zn(NO₃)₂·6H₂O</td>
<td>99.0 minimum</td>
</tr>
<tr>
<td>Maximum impurities</td>
<td></td>
</tr>
</tbody>
</table>
| Insolubles | 0.005  
| Free acid (as HNO₃) | 0.03  
| Chloride (Cl) | 0.005  
| Phosphate (PO₄) | 0.001  
| Sulfate (SO₄) | 0.010  
| Alkalies & Alkaline Earths | 0.20  
| Iron (Fe) | 0.001  
| Lead (Pb) | 0.005  

Physical requirements state that the material be in the form of crys or fragments, and that its color be white or colorless.


**Zirconium Nitrate.** Zn(NO₃)₄·5H₂O, mw 429.33, N 13.05%; white hygr crys or white pieces or scales; decomp at 100°, sol in w and alc. Prepd by the action of nitric acid on Zr oxide (Refs 1, 2 & 3)

The US Dept of Defense Spec for Zirconium Nitrate, Reagent is MIL-Z-11144 (10 May 1951), and specifies the following chemical requirements:

**Nitration**

**I. Introduction**

Nitration is a chemical reaction by which nitro (NO₂) groups are introduced into organic comps. It is basically a substitution or double exchange reaction in which one or more NO₂ groups of the nitrating agent replace one or more groups (usually hydrogen atoms) of the compd being nitrated. It is customary to distinguish three types of nitration reactions as follows:

-C·NO₂:

**O-nitration,** in which a nitro group is attached to an oxygen atom to form a nitrate ester,

-C·ONO₂:

**N-nitration,** in which a nitro group is attached to a nitrogen atom to form a nitramine,

-C·NNO₂
Nitration plays an important role in the prepn of expls. For example, the most commonly used military and commercial expls compds, such as TNT, RDX, NG, EGDN, Tetryl, PETN, NC, and many others are all produced by nitration (chemical names for these and other "common" names are given in Table 1 of Section III).

Nitration reactions are also used to produce many commercially important non-expl organic chemicals and intermediates. In addition to their obvious importance in commerce and synthesis, nitration reactions have contributed greatly to the development of chemical theory — particularly in the formulation of substitution rules for organic compds and the elucidation of reaction mechanisms. Clearly, nitration in all its aspects is a vast subject and much too broad to cover in a single article. In what follows we will therefore limit ourselves primarily to examining nitration from an exploratory point of view. After a brief summary of the Early History of Nitration (Section II), we will list Typical Explosives Produced by Nitration (Section III), enumerate the Nitrating Agents used in producing these and other expls (Section IV), examine Typical Spent Acid Compositions and how they affect yield and waste products (Section V), describe the Nitrating Process both batch and continuous (Section VI), review Nitrating Thermochemistry (Section VII) and Nitrating Mechanisms (Section VIII), briefly summarize Selected Recent Literature on Nitration (Section IX), and conclude with a short discussion of Safety in Nitrations (Section X). The following general refs are highly recommended to the reader requiring greater detail than presented here:

Annual Reviews of Nitration: IEC 40, 1627 (Sept 1948); IEC 41, 1889 (Sept 1949); IEC 42, 1716 (Sept 1950); IEC 43, 1677 (Sept 1951); IEC 44, 2039 (Sept 1952); IEC 45, 1998 (Sept 1953); IEC 46, 1861 (Sept 1954); IEC 47, 1894 (1955); (no review in 1956); IEC 48, 1534 (1957); IEC 50, 1380 (1958); IEC 51, 1123 (1959); IEC 52, 545 (1960); IEC 53, 401 (1961).

T. Urbanski, "Chemistry and Technology of Explosives", Vols 1, 2 & 3 (Refs 74, 75 & 82), an excellent presentation of the prepns, properties and chemistry of nitrated compds and the technology and mechanisms of nitrations.

T.L. Davis, "The Chemistry of Powder and Explosives", (Ref 29), a less detailed, older, but still useful overview of nitrations.


Houben-Weyl, "Methoden der Organischen Chemie, Vierte Auflage (Eugen Müller, Ed), Stickstoff-Verbindungen I, -NO₂ -NO >N=O-, Georg Thiene Verlag, Stuttgart (1971) is a comprehensive modern review of the prepns of nitro compds.

Ph. Naoum, "Nitroglycerin und Nitroglycerin-, sprengstoffe", Springer, Berlin (1924) is the standard reference on NG, EGDN & other nitrates esters.

L.F. Albright & C. Hansen, Eds, "Industrial and Laboratory Nitrations", ACS Symposium Series 22, ACS, Washington, DC (1976). Excellent modern review. Ten chapters emphasize various aspects of the chemistry and mechanism of nitrations, including oxidation and ipso-nitration side reactions. Six chapters discuss the chemistry and physical transfer steps between phases. Eight chapters discuss plant operation-improvements, safety features, and new operations. The final chapter is devoted to vapor phase nitrations.


Refs to nitrated materials, eg Cellulose Nitrate, Cyclonite etc., already described in this Encyclopedia will be found in Sections II & III.

In view of the definition of nitration presented above and the concepts to be developed in Section VIII, discussion of nitrate salts such as H₂NNH₂HNO₃ or CH₂NH₂HNO₃ etc is not included in this article.

II. Early History of Nitration and Nitrated Compounds

According to Urbanski (Ref 74), "Nitration is one of the earliest known organic chemical reactions. It is mentioned in the writings of the alchemists.

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---
As early as in the first half of the XVIIIth century Glauber obtained picric acid by acting on wool and horn with nitric acid. Soon reactions between nitric acid and a variety of organic substances became one of the alchemical reactions most frequently used. They were usually carried out by heating a substance with nitric acid, often to boiling point. Thus picric acid was obtained from certain organic substances such as indigo, silk, resins, etc.

"In 1833 Bracconnot obtained nitric esters of cellulose and starch by acting with nitric acid on plant fibres and starch, at low temperature. In 1834 Mitscherlich nitrated benzene to nitrobenzene. But it is only since 1842, when Zinin reduced nitrobenzene to aniline, that rapid development of the chemistry of nitro compounds and their application to organic industry has occurred."

Indeed it can be stated that the history of modern expls begins with the discoveries of nitroglycerin (NG) and nitrocellulose (or more correctly cellulose nitrate or NC) nearly 125 years ago, and their application to military and commercial usage. An excellent review of the early history of NC is given by T.L. Davis (Ref 29, pp 244–56). The early histories of NG and EGDN (discovered in 1870) are summarized, respectively, in Vol 6, G99-R to G100-R and E259-R, and in the Naofum references cited above.

TNT appears to have been first prepd by Willbrand (Ref 2) in 1863 and its prepn was further developed by Beilstein & Kuhlberg (Ref 3). By the beginning of this century it was already in general use as a military expl.

RDX or Cyclonite was first prepd by Henning (Ref 6) for medicinal use in 1899. Its value as an expl was not recognized until 1920 (Ref 11). Much of the development for its large-scale production was done early in WWII (see Vol 3, C611-L).

PETN was first described in 1894 (Ref 5). Methods for its large-scale production were developed in the late 1920's and early 1930's (Refs 15 & 17).

The use of mixed acid (mixture of nitric and sulfuric acids) as a nitrating agent was first described in 1846 by Muspratt & Hoffman (Ref 1). The sulfuric acid in their mix was considered to be a "dehydrating agent", a view first advanced by Spindler (Ref 4) and developed further by Markovnikov (Ref 7) & Sapozhnikov (Ref 8). The modern concept of the role of sulfuric acid in mixed acid (MA) nitrating agents was first advanced by Hantzsch (Ref 9). Although Hantzsch's ideas are no longer totally accepted, he was the first to point out that in the presence of sulfuric acid (or any acid stronger than nitric) — nitric acid acts as a base in accord with the Brönsted theory of acids and bases. According to Hantzsch:

\[ \text{NO}_2\text{OH} + \text{H}_2\text{SO}_4 = \text{NO(OH)}_2^+ + \text{HSO}_4^- \]

\[ \text{NO}_2\text{OH} + 2\text{H}_2\text{SO}_4 = \text{N(OH)}_3^{+++} + 2\text{HSO}_4^- \]

In their more familiarly written form \( \text{NO(OH)}_2^+ = \text{H}_2\text{NO}_3^+ \) and \( \text{N(OH)}_3^{+++} = \text{H}_3\text{NO}_3^+ \) are respectively the nitricidium and hydronitricidium ions. For further discussion of early theories of species existing in MA the reader is referred to Urbanski (Ref 74, pp 12–14). Modern concepts will be examined in detail in Section VIII.

Early nitrating theories considered nitration as an addition reaction in which the initial step was the direct addition of the nitrating agent to the molecule undergoing nitration, eg:

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

These theories are reviewed in Urbanski (Ref 74, pp53–60). Modern views of the mechanism of nitrination will be examined in detail in Section VIII.

III. Typical Explosives Produced by Nitrination

As already mentioned (Section I), the prepns of most of the commonly used high expl compds involves one or more nitration reactions. Indeed, except for ammonium nitrate (AN), primary expls, and BKpdr, it is difficult to bring to mind any expl in common use (or even a laboratory curiosity) that was not prepared by nitrination. In Table 1, we list the most important military and commercial high expl compds produced by nitrination. We have grouped these compds by nitrination type, ie C-nitrination, O-nitrination, and N-nitrination. Note that either nitric acid or mixed acid are the nitrating agents principally employed in industry. This will be discussed further in the next section. The Table also gives Encyclopedia references for those compounds already described in previous Encyclopedia volumes.
### Table 1

**Some Typical Explosive Compounds Produced by Nitrination**

#### C-Nitrination

<table>
<thead>
<tr>
<th>Compound</th>
<th>Common Name or Abbreviation</th>
<th>Usual Nitrating Agent*</th>
<th>Encyclopedia Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinitrotoluene</td>
<td>TNT**</td>
<td>MA</td>
<td></td>
</tr>
<tr>
<td>Hexanitrostilbene</td>
<td>HNS</td>
<td>MA</td>
<td>Vol 5, D1456-R (f)</td>
</tr>
<tr>
<td>Trinitrophenol</td>
<td>Picric Acid</td>
<td>NA (a)</td>
<td></td>
</tr>
<tr>
<td>Trinitroresorcinol</td>
<td>Styphnic Acid</td>
<td>NA (a)</td>
<td>Vol 5, D1276-R (g)</td>
</tr>
<tr>
<td>Hexanitrodiphenylamine</td>
<td>Hexyl</td>
<td>NA or MA</td>
<td>Vol 5, D1434-R</td>
</tr>
<tr>
<td>1,3 Diamino-2,4,6-</td>
<td>DATB</td>
<td>NA</td>
<td>Vol 5, D1130-R (h)</td>
</tr>
<tr>
<td>Trinitrobenzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitromethane**</td>
<td>NM</td>
<td>NA (b)</td>
<td></td>
</tr>
<tr>
<td>Tetranitromethane</td>
<td>TNM</td>
<td>NA + acet anhyd</td>
<td></td>
</tr>
</tbody>
</table>

#### O-Nitrination

<table>
<thead>
<tr>
<th>Compound</th>
<th>Common Name or Abbreviation</th>
<th>Usual Nitrating Agent*</th>
<th>Encyclopedia Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol trinitrate</td>
<td>NG**</td>
<td>MA</td>
<td>Vol 6, G98-R</td>
</tr>
<tr>
<td>Ethyleneglycoldinitrate</td>
<td>EGDN</td>
<td>MA</td>
<td>Vol 6, E259-R</td>
</tr>
<tr>
<td>Diethyleneglycoldinitrate</td>
<td>DEGDN</td>
<td>MA</td>
<td>Vol 5, D1232-L</td>
</tr>
<tr>
<td>Cellulose nitrate (c)</td>
<td>NC**</td>
<td>NA + acet anhyd</td>
<td>Vol 2, C100-L</td>
</tr>
<tr>
<td>Diethanolnitraminedinitrate (d)</td>
<td>DINA</td>
<td>NA or MA</td>
<td>Vol 5, D1240-R</td>
</tr>
<tr>
<td>Pentarythritoltetranitrate</td>
<td>PETN</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>NS</td>
<td>MA</td>
<td></td>
</tr>
<tr>
<td>Mannitol hexanitrate</td>
<td>Mannitol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### N-Nitrination

<table>
<thead>
<tr>
<th>Compound</th>
<th>Common Name or Abbreviation</th>
<th>Usual Nitrating Agent*</th>
<th>Encyclopedia Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclotrimethylene-</td>
<td>RDX**, Cyclonite</td>
<td>NA + AN</td>
<td>Vol 3, C611-L</td>
</tr>
<tr>
<td>trinitramine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclotetramethylene-</td>
<td>HMX</td>
<td>NA + AN</td>
<td>Vol 3, C605-R</td>
</tr>
<tr>
<td>tetranitramine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylenedinitramine</td>
<td>Haleite, EDNA</td>
<td>NA or MA + acet anhyd</td>
<td>Vol 6, E238-R</td>
</tr>
<tr>
<td>2,4,6 Trinitrophenyl-</td>
<td>Tetryl**</td>
<td>MA</td>
<td></td>
</tr>
<tr>
<td>methyl nitramine (e)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*MA = mixed acid = mixt of nitric & sulfuric acids
NA = nitric acid
AN = ammonium nitrate

**Manufacture discussed in some detail in Section VI
(a) Sulfonation followed by nitration
(b) Vapor phase nitrination
(c) A mixt of the di- & trinitrates
(d) Also an example of N-nitrination
(e) Also an example of C-nitrination
(f) Two moles of TNT condense to form one mole of Hexanitrostilbene
(g) Also see D.A. Salter & R.J. Simkins, GerP 1959930 (1970) & CA 73, 76860 (1970)
(h) Also see J.A. Hoffman & C.F. McDonough, USP 3278604 (1966)
A somewhat unusual type of C-nitration can occur in reactions between nitric acid and unsaturated hydrocarbons. An example of the nitration of unsaturated hydrocarbons is Quilico's scheme (Ref 31) for the formation of nitroform (CH(NO₂)₃):

IV. Nitrating Agents

Nitrating can be carried out either directly by introduction of the nitro group in place of a hydrogen atom or by adding it to a double bond, or else indirectly, by introducing into a compd a group which can readily be replaced by or converted to the nitro group.

The following nitrating agents are most frequently used in industry for the direct introduction of the nitro group:

1. concd nitric acid
2. mixts of concd nitric acid and concd sulfuric acid or oleum in different proportions—these are usually known as "mixed acids," and much less frequently:
3. alkali nitrates in the presence of sulfuoric acid
4. dil nitric acid
5. nitrogen dioxide
6. a soln of nitrogen dioxide in sulfuric acid
7. nitrogen dioxide in the presence of catalysts

For lab preps, and occasionally in industrial use, more expensive nitrating agents may be employed, as for example solns of nitric acid in inert organic solvents (chlor, carbon tetrachloride, eth, nitromethane, etc.), or a soln of nitric acid in phosphoric or acetic acids or in acetic anhydride, trifluoroacetic anhydride or trifluoromethanesulfonic acid (Ref 94).

For nitrating on the lab scale, mixts of nitric acid esters or acyl nitrates, eg acetyl nitrate (CH₃CN0₂) and sulfuric acid may also be used.

Several lesser known nitrating agents, which have been used on a lab scale are metal nitrates in the presence of acetic acid or acetic anhydride, tetranitromethane and hexanitroethane in an alkaline medium, and nitroguanidine in soln in sulfuric acid, used for the nitration of aromatic amines and phenols. For details see Ref 74, Chapt III.

The most common indirect nitration method, often used in nitrating phenols, consists of sulfating the compd and then replacing the sulfo group by a nitro group. The usual nitrating agent for these reactions is concd nitric acid.

Other indirect nitration methods applied on an industrial scale for nitrating phenols involve introducing a nitroso group into the phenol and then oxidizing it into the nitro group. Another method involves the oxidation of a primary amino group to the nitro group.

In expnl work, indirect methods of introducing nitro groups find wide application as, for example, the replacement of a halogen (iodine or bromine in an alkyl iodide or bromide) by the nitro group, by means of silver nitrate (the Victor Meyer reaction).

In aromatic compds, an amino group may be replaced by the nitro group by diazotization and reaction with nitric acid in the presence of cuprous salts (the Sandmeyer reaction). This method is used for lab work only and is described in standard textbooks on preparative organic chemistry.

The most widely used nitrating agents in the prep of important military and commercial high expts are the mixed acids (MA) consisting of various mixts of HNO₃/H₂SO₄/H₂O. Consequently the remainder of this section will be devoted to a discussion of mixed acids. In view of the obvious importance of its use in the prep of military expts, there is a US Military Specification for Mixed Acid (for use in nitration of explosives): MIL-A-50210(MU) (6 December 1968). The "Requirements" for mixed acid prescribed in this specification are:

3.1 Materials. The mixed acid shall be made with sulfuric acid conforming to JAN-A-179, and nitric conforming to JAN-A-183.

3.2 Residue on evaporation. 0.5 percent, max.

3.3 Acid content. As specified by contract or purchase order.

3.4 Total sulfuric acid. As specified by contract or purchase order.

3.5 Total nitric acid. As specified by contract or purchase order.

3.6 Nitrosylsulfuric acid. As specified by contract or purchase order.

3.7 Actual sulfuric. As specified by contract or purchase order.
3.8 Actual nitric acid. As specified by contract or purchase order.

3.9 Water. As specified by contract or purchase order.

The appropriate mixed acid compns for the nitration processes that produce militarily and industrially important expts will be described in Sections V & VI. Typical MA compns in round figures is: 30% HNO₃, 60% H₂SO₄, 10% H₂O. For the nitration of DNT to TNT the MA contains no water and is approx: 20% HNO₃, 80% H₂SO₄.

Nitrate esters such as NG & EGDN are made using MA contg 30–70% HNO₃, 35–70% H₂SO₄ and 0–10% H₂O. The nitric acid content of the MA is usually 20% in excess of stoichiometric.

The ratio of the quantities of components of the nitrating acid (HNO₃, H₂SO₄ and H₂O) is obviously important. The fact that water is formed during the nitration process, thus diluting the nitrating mixt, must be taken into consideration. Since sulfuric acid is the principal “dehydrating” component of MA, the amount of H₂SO₄ must be chosen in such a proportion that it can take up most of the matter formed during the nitration. Otherwise nitration might be incomplete. A commonly used measure of the effectiveness of the sulfuric acid in doing this is the DVS or dehydrating value of sulfuric acid.

DVS = \( \frac{\text{H}_2\text{SO}_4}{(\text{H}_2\text{O})_t + (\text{H}_2\text{O})_f} \)

where (H₂O)ₜ is the initial concn of water in the nitrating mixt before nitrating and (H₂O)ᶠ is the concn of water formed during nitration.

The DVS of a given MA should be as high as possible in order to obtain complete nitration. However, as discussed in the next section, compromises must often be made in order to minimize the solubility of the nitrated product in the spent acid, ie, the acid in equilibrium with the nitrated product, as well as the solubility of spent acid in the product.

Gillespie and Miller (Ref 33) arranged various nitrating agents in order of increasing nitration effectiveness, namely:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Effectiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄O₂NO₂</td>
<td>ethyl nitrate</td>
</tr>
<tr>
<td>HNO₃</td>
<td>nitric acid</td>
</tr>
<tr>
<td>CH₃COO·NO₂</td>
<td>acetyl nitrate</td>
</tr>
<tr>
<td>NO₂·NO₂</td>
<td>nitric anhydride</td>
</tr>
<tr>
<td>Cl·NO₂</td>
<td>nitryl chloride</td>
</tr>
<tr>
<td>H₂O·NO₂⁺</td>
<td>nitracidium ion</td>
</tr>
<tr>
<td>NO₂⁺</td>
<td>nitronium ion</td>
</tr>
</tbody>
</table>

According to Urbański (Ref 74, Chapt 2), this order seems to require some alteration. For example, nitryl chloride has been found to be a definitely weaker nitrating agent than nitric acid and should have been placed before it. The nitronium ion, NO₂⁺, occurs in many mixed acid compns.

V. Spent Acid

Acid compns for practical nitration must be formulated in such a manner that the spent acid must:

a) be readily separable from the nitrated product
b) have a minimum solubility for the nitrated product

c) be such that traces of the acid are readily removable from the crude nitrated product
d) be such that traces of product are readily removable from the spent acid

It is obvious that the nitrated product must be separated from the acid in equil with it (spent acid). If the product and the spent acid form two immiscible liq phases, eg, NG, EGDN, or molten TNT, separation is effected by gravity or centrifuging. If the product and spent acid form a solid and a liq phase, eg PA, NC or PETN, separation is effected by centrifuging (PA & NC) or filtration (PETN). If the nitration is carried in the vapor phase (NM), separation is effected by distillation.

To keep product yield at a maximum it is important that the solubility of product in the spent acid be kept to a minimum. This also facilitates removal of traces of product from the spent acid so that it can be either fortified and reused, reused to make lower nitro compds, or neutralized and discharged as non-polluting waste material.

Traces of acid in the product almost always degrade product stability and in some cases can lead to self-ignition and expln. The usual methods of removing traces of spent acid is by washing with water and/or dil alkali solns followed by a water wash.
Typical nitrating acid and spent acid compns used in the manufacture of selected high expls are shown in Table 2.

As illustrations of the loss of yield that can occur if spent acid compns are not adjusted to maintain minimum solubility of product, consider the data in Fig 1. These show a 2–3 fold increase in NG solubility in spent acid contg 7–16% HNO₃ and 16–19% H₂O over that dissolved in spent acid contg 16% HNO₃ and 13–15% H₂O.

Similarly, TNT is very soluble in conc H₂SO₄ as shown in Table 3 (from Ref 19), and considerably less soluble in spent acid contg small amts of nitric acid, as shown in Table 4 (also from Ref 19). According to Orlova (Ref 62), TNT is very soluble (100–800%) in conc HNO₃.

It is also important to minimize the solubility of acid in the product. Fig 2 (from Ref 61) shows the solubility of HNO₃ in NG. The numbers at the right of the curves are the % HNO₃ in the spent acid. The vertical line corresponds to the mole ratio of H₂O/H₂SO₄ to form the monohydrate H₂SO₄·H₂O. Note that the max HNO₃ solubility for each curve occurs close to this vertical line. It is clear that both water content and HNO₃ content of the spent acid should be kept low in order to minimize HNO₃ solubility in the NG.

![Fig 1 Solubility of nitroglycerine in spent acid.](image)

Table 2

<table>
<thead>
<tr>
<th>Product</th>
<th>Nitrating Acid (%)</th>
<th>Spent Acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNT (a)</td>
<td>28/56/16 HNO₃/H₂SO₄/H₂O</td>
<td>70/30 H₂SO₄/H₂O</td>
</tr>
<tr>
<td>DNT (a)</td>
<td>28/64/8 HNO₃/H₂SO₄/H₂O</td>
<td>2/76/22 HNO₃/H₂SO₄/H₂O</td>
</tr>
<tr>
<td>TNT (a)</td>
<td>20/80 HNO₃/H₂SO₄</td>
<td>4/86/10 HNO₃/H₂SO₄/H₂O</td>
</tr>
<tr>
<td>TNT (b)</td>
<td>8/90/2 HNO₃/H₂SO₄/H₂O</td>
<td>4/76/18/2</td>
</tr>
<tr>
<td>PA (a) (c)</td>
<td>70/20/10 HNO₃/H₂SO₄/H₂O</td>
<td>HNO₃/H₂SO₄/H₂O/other</td>
</tr>
<tr>
<td>NG (a)</td>
<td>50/50 HNO₃/H₂SO₄</td>
<td>13/71/16 HNO₃/H₂SO₄/H₂O</td>
</tr>
<tr>
<td>NG (b)</td>
<td>50/50 HNO₃/H₂SO₄</td>
<td>–</td>
</tr>
<tr>
<td>DEGDN (a)</td>
<td>65/35 HNO₃/H₂SO₄</td>
<td>29/45/22/4 HNO₃/H₂SO₄/H₂O/DEGDN</td>
</tr>
<tr>
<td>PETN (a)</td>
<td>99/1 HNO₃/H₂O</td>
<td>30/70 HNO₃/H₂O (d)</td>
</tr>
<tr>
<td>NC (a)</td>
<td>22/68/9 HNO₃/H₂SO₄/H₂O</td>
<td>19/70/11 HNO₃/H₂SO₄/H₂O</td>
</tr>
<tr>
<td>Tetryl (a)</td>
<td>78/6/16 HNO₃/H₂SO₄/H₂O</td>
<td>1/0/5/82.5/16 HNO₃/NO₂/H₂SO₄/H₂O</td>
</tr>
</tbody>
</table>

*These are approximate "average” compns for several different processes.

(a) Batch nitratio  (b) Continuous nitratio   (c) Final step  (d) Water is added to ppt PETN.
### Table 3

**SOLUBILITY OF α-TRINITROTOLUENE IN SULFURIC ACID (IN %)**

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Concentration of H₂SO₄, %</th>
<th>70</th>
<th>75</th>
<th>80</th>
<th>85</th>
<th>90</th>
<th>95</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>–</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>2.0</td>
<td>3.5</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>0.3</td>
<td>0.45</td>
<td>0.75</td>
<td>2.2</td>
<td>4.0</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>–</td>
<td>0.3</td>
<td>0.50</td>
<td>0.85</td>
<td>2.5</td>
<td>4.8</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>–</td>
<td>0.32</td>
<td>0.55</td>
<td>0.95</td>
<td>2.6</td>
<td>5.2</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>–</td>
<td>0.35</td>
<td>0.60</td>
<td>1.0</td>
<td>2.7</td>
<td>6.0</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.2</td>
<td>0.4</td>
<td>0.65</td>
<td>1.3</td>
<td>3.0</td>
<td>7.0</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.2</td>
<td>0.45</td>
<td>0.70</td>
<td>1.7</td>
<td>3.5</td>
<td>8.5</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.22</td>
<td>0.50</td>
<td>1.0</td>
<td>2.3</td>
<td>5.2</td>
<td>11.0</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.35</td>
<td>0.7</td>
<td>1.6</td>
<td>3.3</td>
<td>7.0</td>
<td>13.5</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.6</td>
<td>1.3</td>
<td>2.4</td>
<td>4.8</td>
<td>10.0</td>
<td>18.0</td>
<td>26.5</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4

**SOLUBILITY OF α-TRINITROTOLUENE IN MIXED ACID**

<table>
<thead>
<tr>
<th>Composition of the mixture, %</th>
<th>Solubility, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 20°C</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>HNO₃</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
</tr>
</tbody>
</table>
and RDX and Tetral, examples of N-nitrination. NG, NC and RDX (cyclonite) production has already been described in previous Encyclopedia articles (see Table 1 of Section III for references): here we shall examine these processes more fully. NM is included because it is a good example of vapor phase nitrination, and because its expl properties have been studied so extensively. (see under Methane and Derivatives in this Vol). In general we will tend to emphasize modern continuous methods since the older batch processes are well described in the literature (eg, in Refs 29, 50, 74, 75 & 82)

TNT. Because TNT is so important in military and commercial use, its manuf will be described in some detail. The nitrination of toluene is carried out in successive stages, eg, Toluene→MNT→DNT→TNT. This method permits the use of spent acid from a higher stage of nitrination, after it has been fortifed with additional nitric acid, for a lower stage nitrination. Moreover, the lower stage nitrations are thus accomplished with less degradation with a MA that has a higher water content than that required for the last nitrination stage, as discussed below.

The presence of a methyl group in toluene greatly facilitates its nitrination as compared with benzene. The reaction of introducing the first nitro group therefore proceeds very quickly, however the methyl group is readily oxidized. Mononitration also leads to oxidation of the ring and the formation of cresols (as in the case of benzene, which is oxidized to phenol). Other oxidation reactions proceed especially readily under drastic conditions which introduce several nitro groups at a high temp.

Sometimes, for example, if the MA is poor in nitric acid, or if an insufficient amount of MA is used, tar formation may take place. For this reason it is preferable to use mixts rich in HNO3, and to use a distinct excess of MA. On the other hand, both excess HNO3 and excess MA favor oxidation processes. Thus a trade-off must be achieved.

Kostevich and Sapozhnikov have carried out extensive studies on the nitrination of toluene to mononitrotoluene, using nitrating mixts of various comps and determining the compn of mixts leading to dinitrotoluene. Their results are shown in the ternary diagram of Fig 3.

Fig 2 Solubility of NG in Spent Acid (Ref 61)

The original ref does not specify the temp at which the data of Fig 2 were obtained, but presumably it was at 20°C since most of the other measurements in their investigation were made at 20°C.

VI. Technology of Nitrination

Industrial nitrations are carried out either in discrete batches or continuously. Modern practice tends to continuous methods, but many nitrated materials are still produced by batch processes. Below, we will describe the technology of manuf of: TNT and NM, examples of C-nitrination: NG and NC, examples of O-nitrination,
An important aspect of nitrating toluene to nitrotoluene is the very low solubility of toluene and nitrotoluenes in nitrating mixts. Therefore the nitration proceeds in a two-phase system and the rate of nitratin depends greatly on dispersion, which in turn depends on keeping the two phases efficiently stirred. This is emphasized in Fig 4, which gives the yield of MNT for a 11/64/25% nitric acid/sulfuric acid/water MA and a nitratin time of 30 minutes as a function of stirring speed.

Fig 3 Nitration of toluene with MA (Kostevich and Sapoznikov, as shown in Ref 74, p 266)

Fig 5 shows the yield of MNT as a function of acid/toluene ratio for a MA of 27/55/18% nitric acid/sulfuric acid/water and a nitratin time of 50 minutes at 30°

The rate of nitratin of toluene to MNT increases with increasing temp, but over the range of 20—75° this rate increase is less than 2-fold (cf Fig 6).

Fig 4 Influence of the rate of stirring on the rate of nitratin of toluene (Orlova, Ref 62)

Fig 5 Change of yield of MNT with the ratio acid/toluene (Orlova, Ref 62)
The nitration of nitrotoluenes to DNT has been studied by Kobe, Skinner & Pringle (Ref 45). Their results are presented in Figs 7a, b and c.

As in the case of MNT, agitation is important in increasing the MNT to DNT nitration rate. Orlova's data for the nitration of p-nitrotoluene with 4/74/23% nitric acid/sulfuric acid/water at 70°C are shown in Fig 8.
Factors affecting the rate of nitrination of DNT \( \rightarrow \) TNT will be discussed in Section VIII. Urbanski (Ref 74) lists several processes for the batchwise manufacture of TNT (e.g., the "French", "British", "USSR" etc). All of them are essentially similar with only minor differences in MA comps and methods of separating the crude TNT from its spent acid. These processes have been largely replaced by continuous nitration techniques. The Biazzi and Bofors continuous processes for the manuf of TNT are described briefly under Continuous Methods of Manufacturing Explosives in Vol 3, C501-L.

The Swedish-Norwegian continuous process and the Hercules process are discussed below.

**Swedish-Norwegian Chematur and Norsk Spraengstoffindustri Continuous Process:** This process, patented in Sweden in 1953 (Ref 42), employs stepwise nitrination of mono- and/or di-nitrotoluene to trinitrotoluene in a series of counter-current units, each unit consisting of a nitrator and a separator.

The principle of design and operation of the unit is given in Fig 9. The nitrator N consists of a U-vessel with two legs or shanks (1) and (2), joined by pipe (6). The components of the

Fig 9  Nitrator for continuous manufacture of TNT (Chematur method, Ref 42)
reaction are introduced thru inlets (4) and (5). Liq can be kept in circulation from leg (1) to leg (2) and back by the turbine-wheel (8) on the drive-shaft (7). By regulating the speed of the turbine (8) and adopting suitable proportions for pipes (3) and (6) it is possible to keep the liq at a higher level in leg (2) than in leg (1). Separator S communicates with the nitrator thru pipe (9). The separator is a rectangular box (10) with a distributor (11) for the mixt coming from the reactor, an outlet (12) for the separated light component and an outlet (13) for the heavy component. At some distance from the inlet, and between the levels of the outlets for the separated components, there is also another outlet (14) for partly separated emulsion. This outlet has adjustable plates (15) and (16) to make it possible to adjust the opening of the outlet with reference to its level in the separator. The partly-separated emulsion is led back to the reactor thru pipe (18) and regulating valve (17). To control the temp of the reaction mixt the unit is equipped with heat exchangers (19) and (20). The separator may also have a heat exchanger jacket, not shown in the diagram.

The unit is operated in the following way: The reactants (see Table 5 for mixed acid compn) are introduced thru inlets (4) and (5), mixed with the help of turbine (8) and circulated thru pipe system (1), (3) and (6), chemical reaction and physical exchange being simultaneously effected. They are continuously transported to the separator in the form of an emulsion. In the separator the components are separated, the light component (nitro compounds) rising to the surface and flowing off continuously thru (12). The heavier spent acid sinks to the bottom and is removed continuously thru (13). In the area between the separated components the partly separated emulsion is withdrawn and led to the mixing part of the reactor. This transport is possible because the level of the liq in the separator thru leg (2) is higher than in leg (1). The rate of feed of partly separated emulsion can be regulated by means of valve (17).

If eighteen nitrating units are used, the compn of the nitrating mixts and the temp during the process will be as shown in Table 5. The multiple unit arrangement is shown in Fig 10.

<table>
<thead>
<tr>
<th>Nitrators Nos.</th>
<th>Composition of nitrating mixtures, %</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HNO₃</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>1-3</td>
<td>0.9</td>
<td>89.2</td>
</tr>
<tr>
<td>4-6</td>
<td>3.0</td>
<td>90.1</td>
</tr>
<tr>
<td>7-9</td>
<td>7.9</td>
<td>87.8</td>
</tr>
<tr>
<td>10-12</td>
<td>7.5</td>
<td>89.8</td>
</tr>
<tr>
<td>13-15</td>
<td>7.5</td>
<td>91.4</td>
</tr>
<tr>
<td>16-18</td>
<td>7.7</td>
<td>91.8</td>
</tr>
</tbody>
</table>
The yield of TNT is as high as 97–99% of theory.

If an unfractionated mix of the mononitrotoluene isomers is used (i.e., the product of straight nitration of toluene), TNT with a mp of 78.7° is produced. If the starting material is free from m-nitrotoluene, TNT with a mp of 80.6° is claimed.

Prime (Ref 73) describes a seven-stage continuous TNT nitrator that has been in operation since 1963. It is based on a joint design by CIL and AB Chematur and is claimed to give yields consistently above 87%. Each nitration stage consists of an agitated U-shaped vessel with the organic phase flowing counter-current to the nitrating acid (similar to the flow sheet in Fig 10).

**Fig 10** Diagram of a system of nitrators (N) and separators (S) in the Chematur method of continuous manufacture of TNT (Ref 42)
10). Most of the nitrated product is in the form of an emulsion and consequently is much safer to handle. The toluene that enters stage 1 leaves stage 7 as crude TNT, while the strong acid that enters stage 7 comes out as weak acid in stage 1. Man-power requirements are kept to a minimum even for 10 million pounds/year production.

**Hercules Continuous Process:** Kouba et al (Ref 60) describe a novel tubular nitration procedure and app by which toluene is nitrated in two stages to form trinitrotoluene. In the first stage of nitration according to this invention, toluene is partially nitrated to an average nitrogen content between about 14.5% and about 16.5%, and in the second stage of nitration partially nitrated toluene is further nitrated to form trinitrotoluene.

They claim that in substantially all of the prior art processes, the operation is really a modified batch process in that high hold-up vessel-type nitrators are employed. Moreover, extensive circulation, recirculation, and a relatively long residence time of the reaction mixture in the nitration zone are characteristics of a majority of the previously proposed methods, and such features are inherently undesirable because they favor degradative side reactions, which occur at all stages of the nitration of toluene to trinitrotoluene, and particularly in the final stage.

Advantages claimed for the Hercules process are: (1) minimization of the amount of nitrated material in the process at any time, (2) rapid nitration with a minimum of side reactions, (3) simplicity of apparatus and equipment, and (4) process is easily controlled.

The essentials of the process are described by: (a) continuously feeding a stream of toluene thru a tubular path to a tubular reaction zone, (b) simultaneously and continuously feeding a stream of nitric acid containing between about 60% and about 85% sulfuric acid, between about 10% and about 30% nitric acid, and between about 3% and about 16% water by weight on a contaminant free basis thru a second tubular path to the tubular reaction zone, (c) impinging the separate streams of toluene and nitrating acid upon each other to form a reaction mixture stream in the tubular reaction, (d) continuously advancing the resultant reaction mixture stream thru the tubular reaction zone while regulating the temperature of the reaction mixture stream between about 40°C and about 140°C until the toluene has been partially nitrated to an average nitrogen content between about 14.5% and about 16.5% by weight, and (e) continuously discharging the reaction mixture stream into a separating zone and there separating spent nitric acid from partially nitrated toluene having an average nitrogen content between about 14.5% and about 16.5% by weight. The above combination of process steps (a) to (e), inclusive, constitutes the first stage of nitration. The partially nitrated toluene product obtained in the first stage of nitration is composed substantially of dinitrotoluene, with relatively minor amounts of mononitrotoluene and trinitrotoluene. It is quite similar in composition to the product hereof known in the art as “Bi-Oil”, employed as an explosive ingredient in various high explosive formulas, and has been found to be a satisfactory equivalent to Bi-Oil as a high-explosive ingredient.

However, for trinitrotoluene manufacture, the partially nitrated toluene is then subjected to a second stage of nitration by (f) continuously feeding a stream of the separated partially nitrated toluene product from step (e) at a temperature above its melting point and under pressure thru a tubular path to a high temperature tubular reaction zone maintained at a temperature between about 90°C and about 140°C, (g) simultaneously and continuously feeding a stream of nitric acid (60–95% H₂SO₄ and 5–40% HNO₃) under pressure thru a second tubular path to the high temperature tubular reaction zone, (h) impinging these separate streams upon each other under pressure in the high temperature reaction zone, (i) continuously advancing the resultant reaction mixture stream under pressure thru the high temperature tubular reaction zone until substantially all of the partially nitrated toluene product has been nitrated to trinitrotoluene, (j) continuously advancing the reaction mixture stream under pressure thru a tubular cooling zone to cool it below about 100°C, and (k) thereafter separating trinitrotoluene from spent nitration acid, the pressure in step (j) being sufficient to prevent any substantial vaporization of nitric acid during the nitration reaction.
In actual practice the temp in the region of the converging streams of the second stage reactor is kept between 90 and 120°, and the rest of the tubular reactor between 110 and 140°. In both stages, turbulent flow of the impinging streams is very desirable. The spent acid of the second stage, upon separation of the TNT, is fortified with aq nitric acid and is reused as the nitrating acid for the first stage.

An important characteristic of this process is that there are no moving parts in either the first-stage or second-stage tubular reactors. "Turbulent flow is relied upon for effectuating intimate dispersion of toluene in first-stage nitrating acid and for effectuating intimate dispersion of partially nitrated toluene and anhydrous tri-nitrating acid in second-stage nitrating, and for maintaining the respective reaction mixtures in emulsified form in their respective tubular reactors. The rates of flow of the reactant feed streams of toluene and first-stage nitrating acid in first-stage nitration and of partially nitrated toluene and anhydrous trinitrating acid in second-stage nitration are regulated so that upon impingement upon each other, they form turbulent reaction mixtures in the respective tubular reactors. No further mixing is required. The first-stage nitration reaction is highly exothermic, commencing immediately upon mixing the toluene with the first-stage nitrating acid and is very rapid, being substantially complete within a matter of 10 seconds or less under the preferred conditions of the invention, and seldom, if ever, requiring any longer than 60 seconds. The second-stage nitration reaction is somewhat slower than first-stage nitration, but is nevertheless quite rapid in comparison to prior art methods, being substantially complete within a matter of from about two to six minutes under the preferred conditions of the invention, and seldom, if ever, requiring longer than about 12 to 15 minutes."

It is claimed (Ref 60) that separation of product and MA in both first and second stages can be accomplished by gravity or by centrifugal separators.

The Hercules continuous TNT process is the basis for three continuous TNT lines which went into operation at the Radford Army Ammunition Plant in Virginia in 1968. The lines were designed by CIL and represent improvements over their plants in Canada, which in turn are improvements over the original AB Chematur process. Details of the actual Radford Continuous TNT Process are described in Refs 86a & 90a.

The most recent UK Royal Ordnance Factory (ROF) continuous process for the manuf of TNT is described by Thomas (Ref 90b). It uses "a novel method of achieving continuous counter-current contacting between heavy and light phases in the trinitration section and some of the washing stages". The plant is also designed to operate based on the use of 96–100% sulfuric acid in the trinitration stage instead of the oleum used at Radford TNT Purification.

Crude TNT produced by either batch or continuous methods requires purification. The ultimate objective of TNT purification is to remove all those products which are more reactive than TNT itself (isomers, nitrocresols, nitrobenzoic acids, etc), or which can easily give oily exudation products, such as isomers or lower nitrated substances.

The oil exudation product (TNT-oil) is very undesirable for the following reasons:

(a) Exudation produces porosity of the TNT charge and reduces its density. This reduces its expl effect. In artillery shells it can produce a dislocation of the charge on firing, compression of the air included in the cavities, and premature expln.

(b) The oily products can penetrate into the threaded parts of the shell and form "fire channels" thru which the ignition of propellant can ignite the charge.

(c) The oily products can penetrate into the detonating fuzes if the explosive of the fuzes is unprotected by a metal envelope, and reduce the detonating power of the fuzes.

In the purification of TNT the following impurities have to be removed: (1) traces of nitric and sulfuric acids; (2) unsymmetrical isomers; (3) products of incomplete nitration; (4) by-products (tetranitromethane, trinitrobenzene, nitrobenzoic acids, nitrocresols, etc).

The first purification step is thorough washing of the TNT with hot water, in washing tanks or by emulsification, followed by neutralization with Na bicarbonate soln. This removes residual acids.
Before WWI neutralized TNT was further purified by crystall from solvents such as mixts of alc and benz. This method added to production cost and increased the fire and expl hazard due to the presence of flammable vapors. Solvent crystall of TNT is no longer used.

Modern purification methods employ Na sulfite solns to react with the β and γ -TNT isomers to form water soluble substances which can then be washed out of the desired α-TNT. However, these water washes form a blood-red soln — the bothersome “red-water” of TNT plants. Modern methods of disposing of “red-water” will be described in Section X.

Nitromethane. The industrial method of producing NM is based on a vapor phase reaction of propane and 70% nitric acid. The reaction is carried out at around 410° and 115–175 psi press. In essence the production of NM involves five steps: 1) nitration; 2) product recovery; 3) product purification; 4) product separation; 5) reactants recovery.

According to Ref 50, nitration is carried out in an “adiabatic” nitrator in which the heat of reaction is utilized to vaporize the nitric acid. A small excess (over stoichiometric) of nitric acid is sprayed thru several nozzles into a stream of hot propane. This excess of nitric acid is kept small in order to minimize oxidative and degradative reactions. The nitrated products are cooled to condense the nitroparaffins and the chamber press is reduced to one atm. The crude products are then scrubbed with a solvent to remove some of the oxidation products. The solvent is then stripped off the crude nitroparaffins in a steam-heated column. The solvent and the oxides of nitrogen in the off gases are recycled. This keeps the yield, based on nitric acid, high — about 90 moles of nitroparaffins per 100 moles of nitric acid. The crude nitroparaffins are decanted from the water that they contain and sent to rectification. The first rectification (distsn) removes any remaining low boiling oxidation products, such as ketones and aldehydes. The nitroparaffins are then treated chemically and water washed, with the wash water then removed by decantation. The final distn is a distn in four successive stages at atm press. The first stage distills off the NM. Nitroethane, 2-nitropropane, and 1-nitropropane are recovered successively in the next three stages. The product distribution is approx 25% NM, 10% nitroethane, 40% 2-nitropropane and 25% 1-nitropropane.

NG. Batch-wise production of NG is described in Vol 6, G99–102, and continuous methods such as the Schmidt-Melssner and Biazzi processes are discussed in Vol 3, C501–505. The Swedish injector process and the Hercules tubular nitrator will be described below, but before doing this we will discuss certain aspects of glycerin nitration that are common to both batch and continuous methods, and then contrast the main features of the batch process vs the continuous process.

The usual MA for batch-wise and early continuous methods of glycerin nitration consists of 45–50% nitric acid and 50–55% sulfuric acid. The MA for the recent continuous methods contains up to 12% water and less nitric acid than above. The MA should be prepd from pure acids, and spent acids are not reused in most installations. The DVS of the MA should be kept high to avoid incompletely nitrated products which are subject to exothermic oxidation reactions. Similarly, it is imperative to maintain the proper MA-to-glycerine ratio. If the amount of glycerine gets to be too high, exothermic decompn and oxidation reactions can occur and temp control becomes most difficult. The proper MA-to-glycerine weight ratio ranges from 5.5 to 6.5.

Effective temp control is an absolute necessity. Small scale nitration can be carried out at temps as high as 40°, but NG yield is reduced at these temps. Low temps favor yield but increase nitration time. In the older methods, temps in the 15–25° range are usually maintained.

In the USA it is common practice to nitrate mixts of glycol and glycerine. These mixed nitrations are essentially similar to pure glycerine nitrations and require no further comment.

The really great advantage of the continuous methods over the batch methods is the much smaller accumulation of NG in any given plant location in the former process. Additional advantages accrue from faster production, better control, lower labor costs, etc. Klassen and Humphrys (Ref 40) compare the Biazzi con-
In a recent review of NG manufacture, Pennie (Ref 66) claims that there are no overwhelming advantages to scrapping operational batch processes and installing continuous equipment. However, in building a new plant, he recommends the installation of a continuous process.

The Swedish Nobel Aktiebolaget process for nitratting glycerine consists of an injector nitratator and a centrifugal separator for separating NG from spent acid. As described in Refs 47, 57 and 75, p 114, the flow of nitratting acid thru an injector sucks in the correct amount of glycerine mixed with air. NG forms an emulsion with the spent acid. After cooling, the emulsion flows into a centrifuge. Here NG is separated from the spent acid and transferred to the washing house.

The main features of this process, which has been in industrial use since 1956, are:

- **Mixed acid** is a mixt of the conventional 50/50 NG-MA and spent acid, such that it contains about 27% nitric acid and 10% water or about 1.7 parts of spent acid to 1 part of MA
- **Glycerine flow** into the injector is controlled by the acid flow (much like the suction in a water aspirator). Thus, if the acid flow is reduced by some equipment malfunctioning, the glycerine flow is automatically decreased.

A novel feature of this process is the **high temp** at which it operates, namely 45–50°. This is achieved by preheating the glycerine (or glycerine-ethylene mixture) to this temp before it enters the injector and cooling the input acid to 0°. The heat of reaction then maintains the fluid temp in the injector in the 45–50° range. Automatic controls give warning or shut down the operation if the temp rises a few degrees above the normal range.

The NG-acid emulsion enters a **cooling system** immediately after leaving the injector and the temp of 45–50° is maintained for only about half a second. During the next 80–90 secs the mixt is cooled to 15°. In the following 30 sec the NG is separated from the spent acid.

A continuous centrifugal separator separates NG from the spent acid. The centrifuge operates at 3200 rpm. For a unit with a capacity of 2500l/hr the quantity of NG in the separator bowl during operation is only 3.5 kg. The separated acid-free NG is emulsified immediately by a wash-jet to form a non-expl mixt and is removed continuously from the separator house to the NG wash-and-weigh house.
The spent acid from the separator contains a small amount of emulsified NG. The portion of spent acid which is to be used to prepare fresh mixed acid need not be separated further, since when nitrating acid is added the emulsified oil redissoles and returns to the cycle.

A flow sheet of the process, as given by Urbanski (Ref 75, his Fig 53), is shown below.

According to Urbanski: "To start the nitration, current from the switch (18) is applied to the electromagnet (6), which closes the air inlet to the injector. Mixed acid is admitted by opening the valve under the acid rotameter (4). The injector now comes into operation. The manometer (13) must show full vacuum. The needle valve (7) is then opened and the vacuum adjusted to about 300mm Hg. The glycerine-glycol mixture is sucked in thru the rotameter (3) to the injector from (2).

The exact setting of the acid and glycerine rotameters is adjusted by means of the corresponding valves and the nitrating temperature is checked. It should be 40–45°C higher than the temperature of the incoming mixed acid.

Through the inspection glass, nitroglycerine can be seen leaving the separator within about 2 mins after nitrates has begun.

To stop the process the circuit through the electromagnet (6) is broken at (18), so that air rushes into the injector and the glycerine in the pipe and in rotameter (3) runs back to (2). Mixed acid should be allowed to flow for 1 min in order to flush the pipes and cooling system. The separator is stopped about 10 min later and empties automatically.

The contents of the separator are collected in a special small separation vessel. The emulsified explosive oil is separated and delivered.

Fig. 53. Flow sheet of injector nitration of glycerine and centrifugal separation of nitroglycerine at Gyttorp (Nitroglycerin Aktiebolaget Gyttorp, Sweden): 1 and 9—tubular coolers (–12°C), 2—glycerine suction tank with a constant level, 3—glycerine rotameter, 4—acid rotameter, 5—injector-nitrator, 6—electromagnet, 7—needle valve for the air inlet to the injector, 8—cold water cooler, 10—injector to supply nitroglycerine-water emulsion, 11—rotameter supplying water to 10, 12, 14, 15—thermometers, 13—vacuum-meter, 16—glass thermometer, 17—alarm bell, 18—current switch, 19—relay to electromagnet 6.
Fig. 59. Flow-sheet of washing nitroglycerine at Gyttorp: A—separator of acid wash-water, B—separator of alkaline wash-water, C—separator of warm wash-water, D—storage tanks, with washing equipment, E—storage tanks with refrigerating coils, F—nitroglycerine wagon on a balance, 1, 4, 7—air separators, 2, 5—injectors, 3, 6, 9—wash-columns.

direct to the wash jet (10). After rinsing with separated spent acid, the separator is ready to be restarted.

Urbanski describes the washing procedure as follows:

"Continuous washing of nitroglycerine is carried out in three wash columns: (3), (6), and (9) (his Fig 59)."

Operating characteristics of the Gyttorp injection nitratrator are: production: 500–650kg NG/hr; acid consumption: 2600–3400kg/hr; glycercine consumption: 216–281kg/hr; and the yield of NG-nitroglycerol mixt is 231–232.5kg of expl oil, ie, 93.9–94.5% of theoretical.

Hercules Tubular Nitratrator. Like the Gyttorp injection nitratrator, the Hercules tubular nitratrator involves no mechanical mixing devices and thus minimizes impact and friction hazards during nitration. It also operates on a very short nitration cycle, thus minimizing side reactions and producing exceptionally pure products. Further advantages of the tubular nitratrator (again similar to the injector process) are minimum amounts of product in process at any time, positive control of the reagents and relatively inexpensive equipment. McKinney's basic patent (Ref 59) describes the process as follows:

"Generally described, the continuous manufacture of explosive liquid nitric acid esters of polyhydric alcohols in accordance with this invention comprises continuously feeding a stream of polyhydric alcohol through a tubular path to a tubular reaction zone, simultaneously and continuously feeding a stream of precooled nitrating acid through a second tubular path to the tubular reaction zone, causing the separate streams of polyhydric alcohol and precooled nitrating acid to impinge upon each other at sufficient flow rates to form a turbulent reaction mixture stream in the tubular reaction zone, continuously advancing the resultant reaction mixture stream through the tubular reaction zone at a flow rate corresponding to a Reynolds Number of at least about 1000 until substantially all of the polyhydric alcohol has reacted with the nitrating acid to form explosive liquid nitric acid ester, and thereafter separating explosive liquid nitric acid ester of polyhydric alcohol from spent nitrating acid.

In a preferred embodiment of the invention, the tubular reaction zone is uncooled and the temperature of the reaction mixture in the tubular reaction zone is controlled within safe operating limits by regulating the temperature.
of the precooled nitrating acid and by regulating the proportions, respectively, of the nitrating acid and of the polyhydric alcohol which are mixed together by impingement to form the reaction mixture. Operating with an uncooled tubular reaction zone promotes a more rapid reaction which is desirable, and in fact is an important advantage of the present invention. Moreover, although not necessary in practicing this invention, it has been found desirable to cool the mixture of explosive liquid nitric acid ester and spent nitrating acid upon completion of the nitration reaction and prior to separation, since this promotes a more complete recovery of the product. While cooling can be effected in a separate vessel following discharge of the reaction mixture from the tubular reaction zone, such cooling is more conveniently and efficiently accomplished in a tubular cooling zone forming an extension of the tubular reaction zone. Preferably, but not necessarily, the reaction mixture stream is advanced through the tubular reaction zone, and the tubular cooling zone when employed, at a flow rate corresponding to a Reynolds Number of at least about 2,100 and sufficient to maintain turbulent flow in the reaction mixture”

A simplified flow sheet (taken from the above Patent) is shown below (his Fig 2, and the
operation is described as follows:

"Liquid polyhydric alcohol from supply tank 11 via valved line 12 is fed through metering pump 13 in predetermined proportions via line 14 to tubular reactor 15. Simultaneously, nitrating acid from supply tank 16 via valved line 17 is fed through pump 18 in predetermined proportions via line 19, tubular nitrating acid cooling coil 21, and valved line 24 to tubular reactor 15. 22 is a conventional heat exchange means such as a refrigerating brine bath or the like. Although it is convenient to cool the nitrating acid as illustrated, the invention is not limited in this respect. The only requirement is that the nitrating acid should be cooled before it enters the tubular reaction zone. Accordingly, therefore, cooling means can be employed to cool the nitrating acid at any desirable and convenient point along the path of flow of nitrating acid in the system before the nitrating acid reaches the reaction zone. For example, the nitrating acid can be cooled at supply tank 16, or even at some point before the acid reaches supply tank 16. Valve 23 in line 24 is a throttle valve for regulating the flow of nitrating acid when employing a centrifugal pump. Valve 23 becomes unnecessary when a metering pump or similar constant feed means is employed instead of a centrifugal pump.

Valve 29 in line 14 is a quick opening bypass valve which is normally closed. However, in case of an emergency shutdown, this valve can be instantly opened to shut off the supply of alcohol to the reaction zone and return the alcohol stream via line 31 to alcohol supply tank 11. Such a quick opening by-pass valve normally is not employed in the nitrating acid line, since in case of an emergency shutdown, nitrating acid is employed to sweep out the tubular reactor.

It will be seen from the drawing that feed lines 14 and 24 converge and junction with tubular reactor 15 at one end thereof, and in the embodiment illustrated, the two feed lines and the tubular reactor form a simple T tube section, free of moving parts, obstruction, or constrictions, as illustrated in Fig. 2. The separate streams of polyhydric alcohol and pre-cooled nitrating acid thus converge and impinge upon each other at the point where the two feed lines junction with the tubular reactor."

The nitrating acid for this process contains 18-40% nitric acid, 45-70% sulfuric acid and 11-17% water. The preferred acid-to-glycerine (or glycerine-glycol mixture) ratio is 10 to 20 parts of acid per part of glycerine. Stow, in a later improvement patent (Ref 67) claims an improved mixing "tee" and a more automated continuous cyclic process. He specifies:

"In the preferred practice of this invention, the reaction mixture, upon completion of the nitrating reaction and containing explosive liquid nitric acid ester dispersed in spent nitrating acid, is discharged into a centrifugal separating zone in which spent nitrating acid is continuously separated from acid impure explosive liquid nitric acid ester. Centrifugal separation has a distinct advantage over separation by settling in that only a very small amount of explosive ester is present in concentrated form while in an impure unstable state. Also, during purification of the impure ester it is preferred to centrifugally separate explosive liquid nitric acid ester from washing liquid in order to minimize the quantity of explosive ester in concentrated form at any one time or point during purification".

A further benefit claimed for this process is:

"To achieve the maximum benefits from the present invention, it is preferred to centrifugally separate explosive liquid nitric acid ester from its emulsion in washing liquid in the one or more stages of purification employed in this invention, for by centrifugal separation the amount of explosive liquid nitric acid ester accumulated in concentrated form at any point in the system is reduced to the absolute minimum, particularly since it is preferred to employ the shortest practical lengths of transport pipes between the separators and the injection mixing zones, during which the explosive liquid nitric acid ester is in concentrated form. Since the explosive ester is in emulsified form in washing liquid during transport from the injection mixing zones to the separating zones, there is relatively no danger of detonation. This is because this invention contemplates the use of at least about 2 parts by weight of washing liquid per part of explosive liquid nitric acid ester, and preferably at least about 3 parts washing liquid per part of explosive ester. At 2 parts washing liquid per part of explosive ester, the emulsions of explosive ester in washing liquid are highly insensitive to shock,"
and at ratios of 3:1 or more of washing liquid, such emulsions cannot be detonated."

The centrifugal separator used in conjunction with the tubular nitrator is described in two patents (Refs 53 & 64)

**NC.** Although the nitration of cellulose has been described quite extensively in Vol 2, C100–119, certain aspects of the technical background for its manufacture need amplification.

Commercial NC is not a single chemical entity. Indeed, as shown in Vol 2, C103-L, there are a variety of grades of NC, usually characterized by their nitrogen content. The chemical species that constitute these grades are partially nitrated products and mixtures of the following compounds:

- Cellulose trinitrate \(C_6H_7O_2(ONO_2)_3\) 14.15%N
- Cellulose dinitrate \(C_6H_7O_3(ONO_2)_2\) 11.11%N
- Cellulose mononitrate \(C_6H_7O_4(ONO_2)\) 6.76%N

Thus every NC is composed of anhydroglucose rings with three nitrate groups attached (14.15% N) and of non-nitrated or partially nitrated anhydroglucose rings. Dalmon (Ref 22) succeeded in obtaining almost complete trinitration (14.12% N) by treating cellulose with gaseous \(N_2O_5\).

Many studies, primarily via X-ray patterns, have led to the following picture of NC of varying degree of nitration:

1. Those containing less than 7.5% N show a fiber character and give no X-ray diffraction indicating nitration, but only the pattern of mercerized cellulose.
2. Those containing between 7.5 and 10.5% N are more or less disintegrated, yielding very diffuse diffractions, apparently due in part to very small crystalline elements of mercerized cellulose.
3. Those of more than 10.5% N give diagrams which indicate the crystalline character of the structure. Apparent crystallinity increases as the nitrogen content increases until eventually a critical point at 12.8% is reached when the sharply defined diagram characteristic of cellulose trinitrate makes its appearance. On the basis of these expts the following picture of cellulose nitration emerges. In first stage of nitration (stage I) the nitric acid penetrates the whole of the cellulose structure (otherwise it could not be mercerized), with nitration occurring only in the disordered amorphous regions (stage II). At the same time the micellar arrangement is almost entirely broken down.

Swelling and breakdown of the micellar arrangement takes place in the final stage of nitration (stage III), but to a diminished extent as the acid concn increases. The number of nitrate groups increases with acid concn, but in a random manner, so that crystalline arrangement is at first hindered. It is facilitated as the nitrate groups accumulate, and when 12.8% N is reached there are so many \(NO_2\) groups that an orderly arrangement of chains becomes possible and there is a sudden appearance of the trinitrate structure.

The amorphous part of cellulose is regarded as more reactive than the crystalline part. When the crystalline part enters in a reaction, as for instance in swelling or nitrating, its structure can undergo certain changes, as swelling causes the micelle chains to expand. An outline of the process suggested by Spurlin (Ref 24a) indicating how the micelles react with an esterifying agent is given in Fig 11, which suggests how the reagent attacks one end of the micelle and a gradual sliding apart of the chain ensues.

The grades of NC that are important to the military and commercial explosives industry are guncotton (13.45% N) and dynamite grade NC (12.2% N). The former is primarily used in the manufacture of double-base and high energy propells while the latter is an ingredient of gelatin and semi-gelatin Dynamites. As shown in Fig 12, the nitrogen content of NC can be controlled by the amount of water in the nitrating acid. However, note that guncotton can be obtained with mixed acids having a fairly wide range of water content (at the plateau in the curve). Also note that a "dry" (low water content) MA produces a low nitrogen-content NC.

The above conclusions were also reached in an earlier study by Schiemann & Kühne (Ref 21). Their results, including spent acid compositions, are summarized in Table 7.
Fig 11  Diagram of esterification of cellulose (Spurlin, Ref 24a)

Fig 12  Change of nitrogen content in nitrocellulose as a function of water concentration in nitrating mixtures according to Miles (Ref 44)
Table 7
Change in the mixed acid ratio after nitration

<table>
<thead>
<tr>
<th>Composition of the nitrating mixture, %</th>
<th>Composition of the spent acid, %</th>
<th>Cellulose to acid ratio</th>
<th>Nitrogen content of nitrocellulose, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ H₂SO₄ H₂O</td>
<td>HNO₃ H₂SO₄ H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.78 70.82 5.40</td>
<td>20.69 71.29 8.02</td>
<td>1:50</td>
<td>13.0-13.5</td>
</tr>
<tr>
<td>23.05 68.07 8.88</td>
<td>18.20 69.56 12.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.09 68.52 10.19</td>
<td>16.91 69.10 13.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.65 76.50 0.85</td>
<td>21.80 76.71 1.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.73 73.15 5.12</td>
<td>20.29 74.37 5.34</td>
<td>1:80</td>
<td>12.9-13.5</td>
</tr>
<tr>
<td>20.70 69.45 9.78</td>
<td>19.58 70.12 10.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A concise way of expressing the effect of MA compn on the nitrogen content of the product NC is the so-called Sapozhnikov diagram. Such a diagram, according to Miles & Milborn (Ref 16), is shown in Fig. 13

Fig 13 Sapozhnikov diagram modified by Miles and Milborn.
Composition of acid mixtures in weight %
Treating NC with a mixed acid capable of producing cellulose nitrate with a lower nitrogen value results in a partial denitration of the cellulose. On the other hand, NC immersed in a mixt of concd acids undergoes further nitration. Berl et al. (Ref 18a) have reported that three samples of NC of different nitrogen content, 10.9, 12.7, and 13.5%, respectively, when drowned in two nitrating acids, and immersed for a sufficiently long time, showed the same percentage of nitrogen for each of the three samples of NC immersed in any one of the mixed acids.

Extensive research has been carried out by Wilson and Miles (reported in Ref 44) on the denitration of NC by the mixed acid. They investigated the influence of acids that varied in chemical compn within wide limits (e.g. the content of nitric acid varied from 10 to 70%).

Several noteworthy rules were formulated. Thus, they found that the higher the proportion of nitric acid, the more rapid the rate of denitration. Sulfuric acid alone, or in a mixt containing a small amount of nitric acid (e.g. 6% HNO₃ and 68% of H₂SO₄), has a very weak denitrating effect. The most rapid denitration occurs in the presence of acids able to cause cellulose to swell. The higher the nitrogen content of the substance undergoing denitration, the more rapidly denitrating proceeds. Raising the temp causes the rate of denitration to increase appreciably.

The following example is given: nitrocotton of 12.2% N was denitrated down to 10.7% N at 20°C for 5hrs in acid composed of 69% HNO₃ and 19% H₂O, while at 60°C, denitration to 10.0% N was accomplished within 3 mins.

Urbański (Ref 75, p 340) summarizes the nitration and denitration processes as follows:

"(1) A portion of the cellulose brought into contact with fresh mixed acid is nitrated to a high nitrogen content. The acid is diluted by water produced during the reaction.

(2) Another portion of cellulose not nitrated so as to form a higher nitrated substance, reacts to give a product containing a lower percentage of nitrogen since the mixed acid has been diluted during stage (1). Gradually further dilution of the acid takes place.

(3) Higher nitrated fractions suffer hydrolysis due to the presence of the more dilute acid.

Process (3) may be slow, hence under industrial conditions it may be broken off before equilibrium is established. This means that chemical reaction (3) is not completed. As a final product, a not very homogeneous nitrocotton is obtained. The higher the nitrating temperature, the more rapid the denitration process, the sooner the reaction balance is established, and hence the more uniform the product."

Miles (Ref 44) suggests the following formulae for calculating MA compositions in equilibrium with NC:

$$D_n = \frac{100 - n}{31.13 \frac{R}{N} - R - 1}$$

$$D_w = \frac{40 + w}{31.13 \frac{R}{N} - R - 1}$$

where:

- $N$: nitrogen content of nitrocellulose as % N,
- $n$: the nitric acid concentration in the mixed acid as % HNO₃,
- $w$: the water concentration in the mixed acid as % H₂O,
- $R$: the weight ratio of mixed acid to cellulose,
- $D_n$: the difference in the nitric acid percentage of the mixed acid before and after the nitration,
- $D_w$: the difference in the water percentage in the mixed acid before and after the nitration.
As already stated, the actual manufacture of NC is described in detail in Vol 2. A diagrammatic representation of the Dupont process (typical of US production practice), shown in Fig 14, complements the discussion presented in Vol 2.

A continuous fully automatic nitrating process for producing NC was developed by Hercules, Inc (Ref 55a & Fig 14a). Cellulose and mixed nitrating acid are fed continuously and simultaneously to a vessel where nitrination of the cellulose takes place. After nitra-
tion, the slurry of NC and spent acid is passed continuously into a centrifugal machine. This machine may be considered as divided into zones, and the NC is advanced intermittently from zone to zone. In the first zone most of the original acid from nitration is removed; in each succeeding zone the acid in the NC is displaced with weaker acid, and, finally, in the last zone with water. The operation in all zones proceeds simultaneously. The amount of water used in the final displacement, or wash, is just sufficient so that the effluent will have an acid concentration suitable for the next preceding displacement, and so on until the recovered acid; ultimately leaving the system, approaches the strength of the spent acid from nitration.

Hercules states that the change from batch to continuous nitration involves no change in raw materials, and no change in the nitration reaction. The product of the continuous process is identical with that of the older batch process, except that it is more uniform.

Before proceeding to describe the manufacture of the nitramines, RDX and Tetryl, a few general remarks about the preparation of nitramines are appropriate. Nitramines can be prepared by direct nitrination with anhydrous nitric acid, e.g.:

\[
\text{RCO-\(\text{NH}R\)}_1 + \text{HNO}_3 \rightarrow \text{RCO-\(\text{N}R\)}_1 + \text{O} \quad \text{N}_2 \quad \text{O}_2 \quad \text{CH}_2 \quad \text{R}_1
\]

Where direct nitrination results in degradation, a primary amine can be acylated, nitrated directly to form a secondary nitramine, which is then hydrolyzed to form the primary nitramine as exemplified in the following reaction sequence:

\[
\text{CH}_3\text{NH}_2 + \text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{NH-\(\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{N=NO}_2 \quad \text{NH}_4 \quad \downarrow \quad \text{HCl}
\]

\[
\text{NO}_2 \quad \text{CH}_3\text{NH-\(\text{NO}_2 + \text{NH}_4 \quad \text{Cl}
\]

NH\(_2\) - COOC\(_2\)H\(_5\)

Another method of preparing nitramines is exemplified as follows:

\[
\text{RNHCl + AgNO}_3 \rightarrow \text{RNHNO}_2 + \text{AgCl}
\]

The formation of chloramine as an intermediate, followed by reaction with nitric acid to produce the corresponding nitramine and HOCI, may explain the catalytic action of HCl in the nitrination of amines.

An important preparative method for nitramines is nitrolysis as described by Urbanski (Ref 82, p 13):

"The term 'nitrolysis' is usually applied to a nitrating mechanism in which both the rupture of the C-N bond and the formation of a nitramine occur simultaneously with the formation of an alcohol which subsequently undergoes esterification (1):

\[
\text{RNCH}_2\text{R}_1 + \text{HONO}_2 \rightarrow \text{RN-NO}_2 + \text{HO-CH}_2 \quad \text{R}_1
\]

\[
\text{NO}_2 \quad \text{O} \quad \text{CH}_2 \quad \text{R}_1
\]

Nitrolysis may also proceed without giving rise to alcohol in accordance with Eq (2). Nevertheless, a nitric ester is formed by the possible action of the NO\(_3\)- ion on a free alkyl cation:

\[
\text{R}_2\text{N-CH}_2\text{R}_1 + \text{NO}_3 \rightarrow \text{R}_2\text{N-\(\text{CH}_2\text{R}_1 + \text{NO}_2\)

\[
\text{O}_2\quad \text{N}\quad \text{O} \quad \text{CH}_2 \quad \text{R}_1
\]

and:

"The nitration of hexamethylenetetramine, which contains the grouping -\(\text{CH}_2\text{N-CH}_2\)-\(\text{CH}_2\), is also a nitrolysis reaction. In addition to Cyclonite, a nitrate of methylene glycol is also formed as a result of the cleavage of one of the three linkages between each nitrogen and carbon atom:"

\[
\text{ONO}_2
\]

\[
\text{CH}_2
\]

\[
\text{ONO}_2
\]

Although by our convention the following preparative method is not a nitrination, we include it here for the sake of completeness, since it is used in the preparation of Nitroguanidine and Nitrourea.

\[
\text{RNH}_2 + \text{HONO}_2 \rightarrow \text{RNH}_3\text{NO}_3 \rightarrow \text{RNH-NO}_2
\]

\[
\text{R}_1
\]

\[
\text{NH}_2 + \text{HONO}_3 \rightarrow \text{NH}_2\text{NO}_2 \rightarrow \text{H}_2\text{O}
\]

\[
\text{R}_1
\]

\[
\text{N-NO}_2
\]

All of the above methods are described more fully in Urbanski (Ref 82, pp 8-14)

RDX (Cyclonite). The industrial prepn of RDX is discussed in Vol 3, C612-615. As in the case of NC, this discussion needs to be expanded,
particularly along the lines of presenting more details of the chemistry involved and the effects of process variables.

The chemistry of the prep of RDX is highly complex and remains not fully understood. What follows is a synthesis of the views of British and Canadian investigators (Refs 37a & 41a) as summarized by Urbanski (Ref 82, pp88–89). The following reactions presumably occur when hexamine is treated with nitric acid to produce RDX:

\[
\begin{align*}
\text{CH}_2 & \quad \text{N} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{H}_2 \text{C} & \quad \text{N} \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
& \quad \text{HNO}_3 \\
\end{align*}
\]

Hexamine

\[
\begin{align*}
\text{CH}_2 & \quad \text{N} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{H}_2 \text{C} & \quad \text{N} \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
& \quad \text{NHNO}_3 \\
\end{align*}
\]

Hexamine Dinitrate

\[
\begin{align*}
\text{NO}_2 & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{H}_2 \text{C} & \quad \text{N} \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
& \quad \text{NHNO}_3 \\
\end{align*}
\]

Compound I

Compound I is formed from Hexamine Dinitrate via nitrolysis.

Further nitrolysis (with cleavage of bond A) forms a hypothetical compound (compound II) as follows:

\[
\begin{align*}
\text{NO}_3 & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{NNO}_2 \text{CH}_2 & \quad \text{NCH}_2 \text{ONO}_2 \\
\text{CH}_2 & \quad \text{N} \\
\end{align*}
\]

Compound II

(Hypothetical)

Compound II now undergoes further nitrolysis (with cleavage of bond B) to give another hypothetical material, Compound III, and a known material, Compound IV:

\[
\begin{align*}
\text{NO}_2 & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_2 \\
\text{NNO}_2 \text{CH}_2 & \quad \text{NCH}_2 \text{ONO}_2 \\
\text{CH}_2 & \quad \text{N} \\
\end{align*}
\]

Compound III

(Hypothetical)

Compound IV

\[
\begin{align*}
\text{NO}_2 & \quad \text{CH}_2 \\
\text{O}_2 \text{N} & \quad \text{N} \\
\text{CH}_2 & \quad \text{N} \\
\end{align*}
\]

Finally nitrolysis of bond C of compound III yields:

which is RDX. Had bond D been nitrolyzed a chain compound would have been formed. Indeed the prep of RDX is complicated by many side reactions resulting from the nitrolysis of bonds other than those shown in the above sequence (cf Ref 82, pp 89–93). For addnl discussion on the mechanism of nitrolysis of Hexamine, see this Vol under Nuclear Tracers in Explosive Chemistry.

As suggested above, side reactions decrease the yield of RDX. The optimum RDX yield is
about 80% based on hexamine, and about 40% based on formaldehyde (used in making hexamine). Vroom and Winkler (Ref 36d) show that this optimum yield (based on formaldehyde) can be attained using 88 to 97% nitric acid, but the weaker acids require a large acid-to-hexamine ratio (cf fig 15).

Similar results were obtained by Dunning et al (Ref 38a) as shown in Fig 17. Here the yield is based on Hexamine. Note that with 85% nitric acid, optimum RDX yield appears to be unachievable.

Fig 15 Effect of nitric acid–hexamine ratio on initial rate of cyclonite formation at 0°C, according to Vroom and Winkler (Ref 36d).

Fig 17 Rate of nitration of hexamine at 0°C with various concentrations of nitric acid, according to Dunning, Millard and Nutt (Ref 38a).

A faster nitration is also achieved when nearly anhydrous nitric acid is used (cf Fig 16).

Fig 16 Effect of nitric acid–hexamine ratio on final yield of cyclonite, according to Vroom and Winkler (Ref 36d).

A description of the various RDX manufacturing processes is given in the Vol 3 ref cited above. Urbanski (Ref 82, pp 104–113) gives the following material balances for these processes:

British process: To produce 1000kg of RDX, 833kg of Hexamine and 8779kg of HNO₃ are required: 3482kg of dil 55% HNO₃ are recovered plus 3429kg of HNO₃ from the absorption towers. Thus the net consumption of HNO₃ for nitration is 1868kg. In addition, 490kg of H₂SO₄ are used for the concn of HNO₃.

SH process: To produce 1000kg of RDX, 880kg of Hexamine and 6800–7760kg of 99% nitric acid are required. The net consumption of nitric acid is 1720–1850kg; 5080–5850kg of 99% HNO₃ are recovered.

K process: To produce 1000kg of RDX, 480–500kg of Hexamine, 8600kg of HNO₃, and 4500kg of AN are required. The consumption of HNO₃ and AN is 1400kg and 1200kg respectively. Recovery amounts to 7200kg of HNO₃ and 3600kg of AN.
**E process:** To produce 1000kg of RDX, 630–635kg of paraformaldehyde, 1800kg AN, 5000–5100kg of acetic anhydride, containing 19kg of boron fluoride are required. The consumption of acetic anhydride amounts to about 800kg.

**KA process:** To produce 1000kg of RDX, 400kg of Hexamine, 430kg of AN, 680kg of 99% HNO₃ and 2400kg of acetic anhydride are required. About 450kg of acetic anhydride are consumed.

The material balance for the Bachmann process is similar to that of the KA process.

**Tetryl.** In the manufacture of Tetryl, it is usual not to nitrate dimethylaniline directly, but to dissolve it first in concd sulfuric acid and then to nitrate the dimethylaniline sulfate so obtained. Direct nitrination of dimethylaniline proceeds so violently that it can be carried out only under specialized conditions. Many years experience of Tetryl manufacture has shown that the ratio of sulfuric acid to dimethylaniline should not be lower than 3:1, since a smaller amount of sulfuric acid may be detrimental to the nitrination process. However, the ratio of sulfuric acid to dimethylaniline must not be too high, otherwise Tetryl yield is decreased. Temp must be maintained between 20–45°C to avoid sulfonation of the benzene ring. Care must be exercised not to leave any unreacted dimethylaniline prior to introduction of nitric acid, because of the potential violence of the dimethylaniline-nitric acid reaction. Consequently, continuous methods of prep'n are to be preferred as they inherently minimize accumulation of unreacted dimethylaniline.

A diagrammatic representation of a continuous process for the production of Tetryl is shown in Fig 18. According to Urbanski (Ref 82, p 58):

"The nitrating acid is metered in the dosing tank (1) and the dimethylaniline soln in the dosing tank (2). Both liquids are introduced into the nitrator I, their rate of inflow being so regulated that 15.4 parts of the dimethylaniline soln in sulfuric acid mix with 9.2 parts of nitrating mix composed of: HNO₃, 67%; H₂SO₄, 16%; and H₂O, 17%. The contents of the nitrator are heated to a temp of 68°C, heating is then discontinued, and the temp in the nitrator maintained at 60–72°C. The nitrator is cooled externally, if necessary. For safe and efficient nitration very vigorous stirring is essential to ensure that the reacting liquids are mixed almost instantaneously. Since the mixt is kept in nitrator I for a very short period, reaction may be incomplete. Its contents are discharged via an overfall to a larger reactor II, also provided with a stirrer. In reactor II the same temp (70°C) is maintained by heating. Here the reaction is completed and the liq, together with the partly crystallized product, is allowed to run into crystallizer (3) in which the whole is cooled to 20°C and afterwards discharged to the vacuum filter (4). Tetryl is collected on the filter and the spent acid is passed on to be denitrated."

The filtered product is then thoroughly washed with water and crystallized from a benz or acet soln. For details see Ref 82, pp 59–61.

An alternate, two-stage method of producing Tetryl is used in Germany. In the first stage dinitromethylamine is prep'd by reacting chlorodinitrobenzene with methyamine in the presence of Na hydroxide. In the second stage the dinitromethylamine is nitrated in a similar manner as above to produce Tetryl. The dinitromethylamine is first dissolved in sulfuric acid (which is made from spent acid and contains some nitric acid, oxides of nitrogen, and 16%
water) and then poured into mixed acid consisting of 78/6/16 nitric acid/sulfuric acid/water.

A lab study describes the formation of Tetryl from dimethylaniline proceeding in two main stages: (1) dimethylaniline → 2,4-dinitrodimethylaniline, and (2) 2,4-dinitromethylaniline → Tetryl, the latter stage proceeding largely via 2,4-dinitromonomethylaniline, but also via dimethylnicotamide (Ref 36e).

VII. Thermochemistry of Nitration

Since nitration is exothermic reactions it is necessary to provide some means of heat control to prevent run-aways. The simplest method is to use a large excess of nitrating agent and have it act as a heat sink. This is often impractical and precooling the reagents and/or heat removal during reaction are frequently employed. Thermochemical calculations are consequently most useful in determining how much heat is evolved in a particular nitration and how much heat must be removed to keep the reaction at an acceptable temp level.

Sources of thermochemical data for such calculations are: Vol 7, H38-Lff: “Heat Effects—Data for Common Explosives”; NBS Circular 500 (Ref 39a); Cox & Plisher (Ref 89); and the studies of Rhodes & Nelson (Ref 24b) and McKinley & Brown (Ref 28a) on mixed acids.

As an example of such a calculation we will compute the heat evolution and temp rise occurring during the mixed acid nitration of glycerol to NG. We will assume that a typical 50/50 nitric acid/sulfuric acid MA is used and that the MA/glycerol ratio is 5/1. Further assumptions are that all the glycerol is converted to NG, and that the heats of soln of NG in the spent acid, and of spent acid in the NG, are negligibly small (cf discussion of these effects by the writer in Ref 51). The net reaction is then:

\[ \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{HNO}_3 \rightarrow 3\text{HNO}_3 + 2.35\text{H}_2\text{SO}_4 + \text{NG} \]

The spent acid compn is 12.6/70/8/16.6 nitric acid/sulfuric acid/water, or 83.4% total acid and 15.1% nitric acid based on total acid. The total heat of reaction \( \Delta H \) is \( \Delta H_n + \Delta H_d \) where \( \Delta H_n \) is the heat of nitation, i.e., the heat of reaction for:

\[ \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{HNO}_3 \rightarrow \text{NG} + 3\text{H}_2\text{O} \text{(liq)} \]

and \( \Delta H_d \) is the heat of dilution for the 50/50 MA being converted into the 12.6/70/8/16.6 spent acid. As shown in Vol 7, H38-Lff, \( \Delta H_n = -9.4 \text{kcal/mole for glycerol (negative } \Delta H \text{'s indicate exothermic reactions). According to Figs 19 and 20, taken from McKinley & Brown (Ref 28a), } \Delta H_d \text{ is obtained as follows: the enthalpy of 460g of 50/50 MA (the amount used per mole of glycerol) at } 25^\circ \text{ is}

\[ 0.460 \times [(-14.5+25-0)0.405] = -2.03 \text{kcal} \]

and the enthalpy of 325g of 12.6/70/8/16.6 spent acid is

\[ 0.325[-55.0+(25-0)0.45] = -14.25 \text{kcal} \]

The positive terms in these equations are the \( c_p \Delta T \) terms to convert the enthalpies from 0\(^\circ\) to 25\(^\circ\) to make the \( \Delta H_d \) consistent with \( \Delta H_n \) which is for 25\(^\circ\). The difference in enthalpies of the spent acid and MA is \( \Delta H_d = -12.2 \text{kcal} \). Then \( \Delta H_n = \Delta H_n + \Delta H_d = -21.6 \text{kcal per mole of glycerol or } -234 \text{kcal per kg of glycerol. Note that for NG the heat of dilution is greater than the heat of nitation.}

Urbaniski (Ref 74, p 146) gives \( \Delta H_n = -252 \text{kcal per kg of glycerol without showing how this value was obtained. Fig 19 is not easy to use and it contains rather old but apparently reliable data. An upper limit estimate to check the validity of the above calculation is readily obtained by assuming that the total heat effect of dilution is due to the dilution of sulfuric acid by the water formed during the reaction. Using the accurately known heats of dilution of sulfuric acid (Ref 39a), \( \Delta H_d = -18.7 \text{kcal} \) for 2.35 moles of H\(_2\)SO\(_4\) diluted by 3.00 moles of H\(_2\)O. Thus an upper limit estimate for \( \Delta H_n = -28.1 \text{kcal/mole glycerol and a specific heat of 0.45cal/g for the spent acid and 0.36cal/g for the NG (from the above cited Vol 7 reference)} \]

\[ \Delta T = 21.6 \times 10^3 \text{ } / \left(0.36 \times 227 + 0.45 \times 325\right) = 156^\circ \]

This is of course much higher than permissible (max nitation temps should be less than 50\(^\circ\)) and means of heat removal or cooling must therefore be provided.

Additional total heats of nitation quoted by Urbaniski (but without details of how they are obtained) are:
Fig 19  Enthalpy of nitric acid, sulfuric acid, and water mixtures
McKinley and Brown (Ref 28a)
Picric Acid: $-917.4\text{ kcal/kg of phenol}$ (Ref 74, p 146)

NC: 10.4 to 10.6% N; $-6.9$ to $-7.8\text{ kcal/kg}$ of cellulose; 13.3% N; $-11.4\text{ kcal/kg}$ of cellulose (Ref 75, p 358)

Several exptl studies are quoted for the heat of nitrating one OH group. On a per mole basis these range from 1.7 to 2.1 kcal/mole. However, Miles (Ref 44) computes a lower value, 1.2 kcal/mole, on the basis of accurately determined heats of combustion of NC.

**RDX.** Gilpin & Winkler (Ref 38b) measured a heat of nitration of $-88.0\text{ kcal/mole}$ of hexamine for the reaction of hexamine with 97.5% nitric acid. They also obtained a value of $-140\text{ kcal/mole}$ of hexamine for the formation of RDX from hexamine and Bachmann reagents (acetic anhydride, acetic acid, ammonium nitrate and nitric acid). Incidentally, Gilpin & Winkler interpret their results to mean that hexamine dinitrate is an intermediate in the direct nitrolysis of hexamine to give RDX, while hexamine mononitrate is an intermediate in the Bachmann process of producing RDX.

Dunning et al (Ref 38a) give the heat of reaction, per mole of hexamine, for the formation of RDX at several acid concns at 20° and at $-35.5°$. Their results are shown in Fig 21. Comparison of their data with those of Gilpin and Winkler shows that their heat effect is almost 10 kcal/mole greater than that reported by Gilpin & Winkler (Ref 38b).

Fig 21 1—Nitration of hexamine at 20°C; 2—nitration of hexamine at $-35.5°C$, according to Dunning, Millard and Nutt (Ref 38a)
VIII. Nitration Mechanisms

Summary. Modern views of the mechanism of nitration are divided into two schools. Ingold and co-workers champion the concept that nitration is primarily ionic in character and its rate-determining step (at least in a concd nitrating acid medium) involves the nitronium ion, thus:

$$\text{RH} + \text{NO}_2^+ \rightarrow \overset{\text{slow}}{\underset{\text{fast}}{\text{R}^+ + \text{HNO}_2^+}}$$

for C-nitrations;

$$\text{R}_3\text{COH} + \text{NO}_2^+ \rightarrow \overset{\text{slow}}{\underset{\text{fast}}{\text{R}_3\text{C}^+ + \text{HNO}_2^+}}$$

for O-nitrations; and

$$\text{R}_3\text{N}^+ + \text{NO}_2^+ \rightarrow \overset{\text{slow}}{\underset{\text{fast}}{\text{R}_3\text{N}^+ + \text{NO}_2^+ + \text{HNO}_3}}$$

for N-nitrations.

Titov and co-workers, although conceding the validity of the ionic nitration mechanism for liq phase nitrations with concd acids, believe that many nitrations occur via a free-radical mechanism involving the free radicals (at any rate molecules having an unpaired electron) NO₂, NO₃, and NO. For vapor phase nitration of hydrocarbons, nitration of side chains of aromatic compds in solvents, and the nitration of olefins in nonpolar solvents, the Titov Mechanism is:

$$\overset{\text{slow}}{\underset{\text{fast}}{\text{RH} + \text{HNO}_3 \rightarrow \text{R}^+ + \text{HNO}_2}}$$

followed by $\text{R}^+ + \text{NO}_2 \rightarrow \text{RNO}_2$. According to Titov the formation of the reactive $\dot{R}$ radicals explains the many side reactions (eg oxidations, nitrosations etc) observed in hydrocarbon nitrations.

The main differences between the ionic and free radical schools are in their respective views of:

a) Nitrations with moderately dil nitric acid
b) Vapor phase nitrations with nitric acid
c) The roles of NO and/or HNO₂ in nitrations

We will examine both schools of thought below, but before doing this we need to examine the compn (ie, the species present) in such nitratng mediums as mixed acid, nitric acid, and oxides of nitrogen.

Composition of Nitrating Media

Early concepts of the composition of mixed acids were described in Section II. More recent concepts are best summarized by the following equilibria:

$$\text{HNO}_3 + \text{H}_2\text{SO}_4 = \text{H}_2\text{NO}_3^+ + \text{HSO}_4^- \quad (1)$$

$$\text{H}_2\text{SO}_4 = \text{H}_3\text{O}^+ + \text{HSO}_4^- \quad (2)$$

$$\text{H}_2\text{NO}_3^+ + \text{H}_2\text{SO}_4 = \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_3\text{O}^+ \quad (3)$$

Steps (1) and (2) are fast while the production of nitronium ion in step (3) is "slow". A great mass of evidence exists in support of the formation of NO₂⁺ in mixed acids of low water content, but there is some controversy about the presence of H₂NO₃⁺ in MA. Hantzsch's cryometric studies (Refs 9 & 18) were interpreted to be in support of the existence of the nitricium ion (H₂NO₃⁺). These views were later supported by the studies of Hammet & co-workers (Refs 20 & 24). Furthermore, Hantzsch isolated crystalline nitricium perchlorate (H₂NO₃⁺)(ClO₄⁻) (Refs 14a & 14b).

Euler was the first to suggest the presence of nitronium ions in mixed acids (Ref 12). This view was later supported by the conductometric studies of Walden (Ref 14). Titov (Ref 28) reinterpreted Hantzsch's data and suggested that the simplest way to explain them was:

$$\text{HNO}_3 + 2\text{H}_2\text{SO}_4 = \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+ \quad (4)$$

ie, step (2) is eliminated and NO₂⁺ is formed via step (4). Ingold et al isolated crystalline nitronium salts (Ref 36b). Raman spectra furnish convincing evidence of the presence of NO₂⁺ in MA. Of particular value are the studies of Chedin et al (Ref 35) which show how NO₂⁺ concn changes with water content of the MA.

Water-free nitric acid is amphoteric, ie, it acts both as an acid and a base, or better as an electron donor or electron acceptor. This view, already suggested in the early Hantzsch papers, was supported by Walden (Ref 14) and later by Dalmon (Ref 30). Then Usanovich (Ref 25) demonstrated that nitric acid acts as a base with sulfuric acid and as an acid with water. Other strong acids (in the general Brönsted sense), such as perchloric acid, phosphoric acid (Ref 25), BF₃ (Ref 26), and HF (Ref 27) make HNO₃ behave as a base, eg:

$$2\text{HF} + \text{HNO}_3 = \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{NO}_3^- \quad (5)$$

Concd nitric acid undergoes "self-ionization". According to Spasokukotskii (Ref 34):

$$3\text{HNO}_3 = \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{NO}_3^- \quad (6)$$
However, more recent investigators (Refs 36, 38 & 49) believe this to be a two stage process, similar to that shown in Eqns 1 & 3:

\[ 2\text{HNO}_3 = \text{H}_2\text{NO}_3^+ + \text{NO}_3^- \quad (7) \]
\[ \text{H}_2\text{NO}_3^+ = \text{NO}_2^+ + \text{H}_2\text{O} \quad (8) \]

Ingold et al (Ref 36) indicate that step (7) is fast and step (8) is "slow."

The studies of Bunton et al (Ref 38) using heavy oxygen (18O) are particularly noteworthy in elucidating the self-ionization process. With moderately "dilute" nitric acid they found that nitration required presence of nitrous acid. Ingold and co-workers (Ref 36c) suggest that the action of nitrous acid is as follows:

\[ \text{HNO}_3 + \text{HNO}_3 = \text{H}_2\text{NO}_3^+ + \text{NO}_3^- \quad (9) \]
\[ \text{H}_2\text{NO}_3^+ = \text{NO}_2^+ + \text{H}_2\text{O} \quad (10) \]
\[ \text{NO}_2^+ + \text{NO}_3^- = \text{N}_2\text{O}_4 \quad (11) \]

Titov (Ref 65) claims that nitric acid also acts as a source of nitrogen oxides via

\[ \text{NO} + \text{HNO}_3 = \text{3NO}_2 + \text{H}_2\text{O} \quad (12) \]

According to Ingold et al (Ref 77) at high temps, in the gas phase:

\[ \text{HONO}_2 = \text{OH} + \text{NO}_2 \quad (13) \]

Nitration can be carried out using \( \text{N}_2\text{O}_5 \) as the nitrating agent. According to Titov (Ref 28) and confirmed by Gillespie et al (Ref 36a):

\[ \text{N}_2\text{O}_5 = \text{NO}_2^+ + \text{NO}_3^- \quad (14) \]

Moreover, as proved by Ogg (Ref 32a):

\[ \text{N}_2\text{O}_5 = \text{NO}_2^- + \text{N}_2\text{O}_3 \quad (15) \]

Thus \( \text{N}_2\text{O}_5 \) can furnish both ionic and free radical species for nitration.

Nitrogen tetroxide dissociates according to:

\[ \text{N}_2\text{O}_4 = 2\text{NO}_2 \]

and thus provides free radical nitrating species. With sulfuric acid:

\[ \text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{NO}_2^+ + \text{HNO}_3 + \text{HSO}_4^- \]

and nitration can then proceed via reactions (1) and (3) to form \( \text{NO}_2^+ \), or via direct reaction with \( \text{NO}_2^- \) and subsequent oxidation of the nitroso compound. Alternatively,

\[ \text{N}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 = \text{NO}^+ + \text{NO}_2^+ + \text{H}_3\text{O}^- + 3\text{HSO}_4^- \]

provides both \( \text{NO}_2^+ \) and \( \text{NO}_2^- \) (Ref 36).

An excellent review of the composition of MA, nitric acid and nitrogen oxides is given by Urbanski (Ref 74, pp 12-52, 102-04)

**Ionic Nitrations**

We shall discuss ionic nitrations mechanisms in terms of nitration by pure nitric acid and where appropriate comment on effects of such additives as sulfuric acid, water, nitrous acid etc. The nitration scheme now generally accepted for liq phase nitration is an electrophilic substitution of the substituting agent on the conjugated 2p electrons of carbon, oxygen or nitrogen atoms. Nitronium ion is the substituting agent *par excellence* for C, O and N-nitrations. The best proofs of these nitration mechanisms come from studies of nitration carried out in solvents — polar, non-polar, or even water. The reaction scheme is as follows:

\[ 2\text{HNO}_3 = \text{H}_2\text{NO}_3^+ + \text{NO}_3^- \quad \text{fast} \quad (7) \]
\[ \text{H}_2\text{NO}_3^+ = \text{NO}_2^+ + \text{H}_2\text{O} \quad \text{slow} \quad (8) \]
\[ \text{NO}_2^+ + \text{XH} = \text{XNO}_2^+ \quad \text{slow} \quad (16) \]
\[ \text{XHNO}_2^+ + \text{NO}_3^- \rightarrow \text{XNO}_2^- + \text{HNO}_3 \quad \text{fast} \quad (17) \]

where X is a benzenehydrocarbons, an alcohol or an amine, and \( \text{NO}_2^+ \) substitution occurs on a ring carbon, alcohol oxygen, or amine nitrogen respectively. Steps (8) or (16) are rate-controlling. Depending on which of these predominates the net reaction is either zero-order or first-order in \( \text{XH} \).

Thus, for a "reactive" \( \text{XH} \) in a not-too-aqueous medium, \( \text{NO}_2^+ \) will be primarily consumed by reaction (16), and the nitration rate will be independent of the concentration, or even the chemical nature, of \( \text{XH} \), i.e., zero-order in \( \text{XH} \). In this case nitration rate will depend on the stationary concen of \( \text{H}_2\text{NO}_3^+ \) and thus in turn on the presence of additives that influence reaction (7), e.g., addition of sulfuric acid will increase (\( \text{H}_2\text{NO}_3^+ \)) via reaction (1), but \( \text{NO}_3^- \) addition will decrease (\( \text{H}_2\text{NO}_3^+ \)) via the reverse of reaction (7).

Conversely, for an "unreactive" \( \text{XH} \), or one present in small concen, or for a highly aq medium, the reverse of reaction (8) prevails over reaction (16), and the rate of nitration now depends on both the nature and concen of \( \text{XH} \), i.e., it is first-order in \( \text{XH} \). The comments made above about \( \text{H}_2\text{SO}_4 \) or \( \text{NO}_3^- \) additives are also applicable to this situation.

The above reaction scheme is largely based on the studies of Ingold's school (Refs 23, 36, 36a, 36b, 36c, 39, 49 & 49a). However, some previous and later investigators, Titov (Ref 28 & 52), Westheimmer and Kharasch (Ref 32), Bennett et al (Ref 32b), Bunton et al (Ref 36c), Bonier & Frizel (Ref 48 & 55), Stromberg & Lecl'chuk (Ref 72) and Chapman et al (Ref 93) also contributed to its elucidation.

The following zero-order rate constants, from Refs 49 & 49a, were obtained in about
A recent investigation (Ref 90) of the 2-stage mixed acid nitration of tetranitroethane (TNE) to hexanitroethane revealed that the nitration was first-order in $\text{NO}_2^+$, TNE and "base" (either $\text{H}_2\text{O}$ or $\text{HSO}_4^-$). The reaction was claimed to proceed via simultaneous attack of $\text{NO}_2^+$ on the C, and of base on the H of the TNE.

As already mentioned, Bunton and Halevi (Ref 38) found that ca 60% nitric acid requires the presence of nitrous acid for it to be a nitration agent. Ingold et al (Ref 36c) postulated the action of nitric acid to proceed via reactions 9, 10 & 11. Now in competition with reaction 11, there may be a nitrosation reaction:

$$\text{XH} + \text{NO}^+ \rightarrow \text{X}^+ \cdot \text{HNO} \rightarrow \text{XNO} + \text{H}^+ \quad (18)$$

followed by

$$\text{XNO} + \text{HNO}_3 \rightarrow \text{XNO}_2 + \text{HNO}_2 \quad (18a)$$

which regenerates nitrous acid. The reaction sequence 9, 10, 11, 18 & 18a may thus explain the nitration mechanism in "dilute" nitric acid. An alternate scheme is proposed by Bonner & Frigel (Ref 55); if strong acids ($\text{HClO}_4$, $\text{H}_2\text{SO}_4$) are present:

$$\text{HNO}_2 + 2\text{HClO}_4 = \text{NO}^+ + \text{H}_2\text{O} + 2\text{ClO}_4^-$$

presumably followed by reactions 18 & 18a.

Several investigators report nitration under conditions where $\text{NO}_2^+$ cannot be present. Amongst these are the studies of Lowen et al (Ref 37), Urbasinski et al (Ref 58) and Brennecke & Kobe (Ref 46), and in particular those of Titov (Refs 28 & 65). These studies suggest the necessity for a non-nitrium nitration mechanism and such a mechanism will be examined in the next subsection.

### Free Radical Nitration

Impure nitric acid can produce $\text{NO}_2$ via reaction (12). Titov (Refs 65 & 39b) also suggests the dehydration reaction for anhydrous nitric acid:

$$3\text{HNO}_3 = \text{N}_2\text{O}_5 + \text{HNO}_3\cdot\text{H}_2\text{O} \quad (19)$$
followed by reaction (15) to form $\text{NO}_2$ and $\text{NO}_3$.

According to Titov, both $\text{NO}_2$ and $\text{NO}_3$ react with $\text{XH}$ as follows:

\[
\begin{align*}
\text{RH} + \text{NO}_2 & \rightarrow \text{R}^+ + \text{HNO}_2 \\
\text{RH} + \text{NO}_3 & \rightarrow \text{R}^+ + \text{HNO}_3
\end{align*}
\]

(20) (21)

and (21) is claimed to be much faster than (20).

However, $\text{N}_2\text{O}_5$ also produces $\text{NO}_2^+$ via reaction (14)

Many reactions, nitration, nitrosation, oxidation, etc are then possible. Titov's generalized scheme is

\[
\begin{align*}
\text{R}-\text{H} & \xrightarrow{\text{NO}_2, \text{NO}_3} \text{R}^+ \\
\text{R} & \xrightarrow{\text{O}^-} \text{R}-\text{O}^- \\
\text{R}-\text{NO}_2 & \xrightarrow{\text{NO}_2, \text{N}_2\text{O}_4} \text{R}-\text{O}^- \text{NO}_2 \\
\text{R}-\text{NO}_3 & \xrightarrow{\text{N}_2\text{O}_4, \text{N}_2\text{O}_5} \text{R}-\text{O}^- \text{NO}_2 \\
\text{R} & \xrightarrow{\text{OH}} \text{HO}^- \\
\text{R}-\text{O}^- \text{NO}_2 & \xrightarrow{\text{O}^-} \text{R}-\text{O}^- \text{O}^- \text{(peroxide radical)}
\end{align*}
\]

Nitric oxide for the above sequence is formed via (12) and/or the decompn of nitric acid produced in (20).

Of course most of the above reaction sequences are possible if one starts with either $\text{N}_2\text{O}_4$ or $\text{N}_2\text{O}_5$ as the nitrating agent.

Titov claims that the free radical mechanism applies for nitration of aliphatic hydrocarbons, of aromatic side chains, of olefins, and of aromatic ring carbons, if in the latter case the nitrating agent is ca. 60–70% nitric acid that is free of nitrous acid, or even more dil acid if oxides of nitrogen are present.

Probably the main point of disagreement between the Ingold and Titov schools arises in the vapor phase nitration of hydrocarbons. Titov believes that this occurs via reaction (19), (20), (21), etc. Ingold et al (Ref 77), on the basis of some sound kinetics, propose the sequence:

\[
\begin{align*}
\text{HNO}_3 & = \text{H}^+ + \text{NO}_2 \\
\text{H}^+ + \text{R} & \rightarrow \text{R}^+ + \text{H}_2\text{O} \\
\text{R}^+ + \text{HNO}_3 & \rightarrow \text{RNO}_2 \text{ (or RONO)} + \text{OH} \\
\text{R}^+ + \text{HNO}_3 & \rightarrow \text{ROH} + \text{NO}_2
\end{align*}
\]

**Reaction Rates in Industrial Nitrations**

It should be pointed out that most of the evidence presented above in support of the nitronium ion or free radical mechanisms of nitration was obtained with homogeneous solns under conditions that cannot be compared directly with the conditions prevailing in industrial nitrations.

Since industrial nitration occurs, in most cases, in two-phase systems a number of workers have investigated the kinetics in both organic and acid phases (Refs 18b, 46 & 81). The consensus is that nitration occurs mainly in the acid phase. In what follows we will examine reaction rate effects in industrial-type nitrations for producing TNT, NG and EGDN.

**TNT:** Reaction rate effects in the production of MNT and DNT were already examined in Section VI. Here we will examine reaction rate effects for the trinitration stage, i.e. DNT $\rightarrow$ TNT.

Orlova (Ref 62) made extensive studies of the conversion of DNT to TNT in mixed acid. Some of her results are shown in Figs 22 thru 25. All the data are for 90°. The mixed acid used in obtaining the results of Fig 23 consists of 16/81/3 nitric acid/sulfuric acid/water, the MA/DNT ratio of 1/5, and reaction time was 40 minutes. These results (Fig 23) should be compared with those shown in Figs 4 & 8.

Orlova summarizes her studies of toluene nitration as follows: Nitration of toluene to MNT and of the latter to DNT under heterogeneous conditions should be considered mainly as a "surface" reaction. This is deduced from the fact that the rate of the reaction depends on the rate of stirring. The reaction of nitration of DNT to TNT in heterogeneous systems is not limited to the surface between the two phases.

This is proved by the fact that the rate of nitration depends very little on the rate of stirring. DNT and nitric acid are distributed between two phases according to their coefficients of distribution and the ratio of the volumes of the two phases. Reaction occurs in both phases but the rate in the acid phase is much higher than in the organic oil phase. This is because the organic oil phase contains only $\text{HNO}_3$ with practically no $\text{H}_2\text{SO}_4$. The rate of nitration of DNT depends therefore largely on the solubility of DNT in the acid layer.

To some extent the organic phase has a nega-
Fig 22 Influence of the concentration of sulfuric acid on the rate of nitration in homogeneous conditions (nitrating mixtures with a high content of HNO₃ (Orlova, Ref 62))

Fig 23 Influence of the rate of stirring on the rate of nitration of DNT (Orlova, Ref 62)

Fig 24 Influence of the content of HNO₃ in nitrating mixtures on the rate of nitration of DNT to TNT (Orlova, Ref 62)

Fig 25 Change of the rate of nitration of DNT in the presence of TNT (Orlova, Ref 62)

tive action on nitration. It is a good solvent for HNO₃ and considerably reduces the concn of HNO₃ in the acid phase

The secondary reactions of oxidation occur in both the organic and acid layers. It is likely that oxidation occurs strongly in the organic layer because of the presence of HNO₃ free of H₂SO₄

The negative influence of the organic layer also consists in reducing the concn of DNT in the acid phase. This occurs when the organic phase is composed mainly of molten TNT.

The distribution coefficient of DNT between the two phases shifts the DNT towards the organic layer. This particular negative action of the TNT layer is less pronounced towards the end of the nitration when very little DNT is left unnitrated. Therefore the most favorable condition of heterogeneous nitration exists at the beginning of the reaction when the organic layer is composed only of DNT. Therefore at this stage of the reaction it is possible to use less concd nitrating mixts and a lower nitration temp.
NG & EGDN

Oehman et al (Ref 56a) suggest that glycerol nitration to NG occurs to some extent on the surface between the acid and "oil" phases. They claim that stirring and/or atomization of the glycerol during its addition increase nitrination rate. However, of primary importance is the ratio of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ in the MA. Optimum rates are achieved for a mole ratio of 1:1 (or somewhat less) corresponding to formation of the hydrate $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$. According to Oehman nitrination becomes slow at a water content corresponding to more than 1.2 moles $\text{H}_2\text{O}$/mole $\text{H}_2\text{SO}_4$. Optimum nitrination temp is around 20°.

Roth, Stow & Koub (Ref 51) investigated the nitrination of ethylene glycol in a tubular nitrator (cf Section VI). Reaction rate was followed by measuring temp rise along the flow path. This furnished data in the form of $\Delta T$ vs time curves such as the one shown in Fig 26.

Since mixing of glycol and MA was very thorough and rapid, this $\Delta T$ mirrors the progress of the exothermic nitrination reaction. Note the strong influence of mixed acid water content on the nitrination rate. This agrees with Oehman et al (Ref 56a), except that Roth et al observed quite rapid nitrination at mole ratios of greater than 1.2/1 $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ where Oehman et al claim slow nitrination.

The data of Fig 26 can be converted into the extent of reaction plot of Fig 27. Fig 27 is a typical first-order plot and this and other data were interpreted to mean that the reaction is pseudo first-order in glycol and nitrination proceeded via a $\text{NO}_2^-$ mechanism.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig26.png}
\caption{Fig 26 Temperature rise in the tubular nitrination of ethylene glycol}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig27.png}
\caption{Fig 27 Extent of EGDN formation as a function of time}
\end{figure}

\section*{IX. Recent Literature on Nitrination}

In recent years there has appeared a considerable volume of literature dealing with nitrations. The expl-oriented publications on nitrations can be divided, albeit somewhat arbitrarily, into three general headings: \textit{nitration mechanisms}, \textit{TNT production}, and \textit{miscellaneous nitrations}, ie, production and prep of expls other than TNT. Studies of nitrination mechanisms were summarized in the preceding section. Recent investigations on expl production and prep via nitrination will be presented below in chronological order.

\textit{TNT Production}

An interesting study by Holahan, Castorina,
Autera & Helf (Ref 63) used carbon-14 tracers to determine the origin of tetranitromethane (TNM) formed during nitration of nitrotoluenes. They found that over 50% of the TNM is derived from the ring carbon attached to the CH₃ group, and over 80% of the TNM comes from m-nitrotoluene. These observations are interpreted in terms of competitive reactions, namely nitrations leading to the formation of TNT and oxidations producing TNM. Since nitration is slowest in the trinitration step it is likely that most of the TNM is formed at this stage. A mechanism is postulated based on the formation of dinitrobenzoic acid from DNT, followed by hydrolysis and nitration to form TNM. Presumably the nitration of either 2,4 or 2,6 DNT m-nitrotoluene is faster than the nitration of m-nitrotoluene-derived DNT, thus permitting more extensive oxidation of the latter.

Nitration vs side-chain oxidation of toluene in dilute MA was investigated by Namba et al (Ref 69). They found that addition of sulfuric acid accelerated both reactions but nitration more than oxidation. Addition of water to the MA favors oxidation as does an increase in reaction temp.

The effects of reactant feeding methods on toluene nitrations were studied by Yamasue et al (Ref 70) in a 15 liter nitrator with a 500rpm agitator. Production of pure MNT or DNT was favored by addition of acid to the toluene or MNT, while in the production of TNT the addition of “oil” to acid is to be preferred, provided sufficient cooling and agitation is available. Purer TNT was produced when the MA contained free SO₃.

R.C. Hauze patented a method of preparing DNT containing a high proportion of the 2,4 isomer (Ref 76). A cycling method using separate moving streams of toluene and mixed acid (eg 20–28% nitric acid, 6–65% sulfuric acid and 8–12% water) is claimed to give consistently high yields of DNT. Product and spent acid are separated by conventional means.

According to Wright et al (Ref 78), nitration of toluene, using a dehydrated, sulfonic acid ion-exchange resin instead of H₂SO₄, with HNO₃ gave decreased ortho/para ratios, which indicated that this type of nitrating agent has a large steric effect. In addition to the normal products, 25–30% of PhCH₂NO₂ was sometimes produced. Ortho/para ratios obtained were 0.68–1.40 depending upon reaction conditions such as: temp, solvent, the stoichiometry (ie, resin/HNO₃ ratio), and the amount H₂O present. In addition to the three nitrotoluenes, BzH, PhCH₂OH and PhCH₂NO₂ were identified.

Picard et al (Ref 80) patented a method of nitrating toluene with HNO₃ and BF₃ to form DNT and TNT. Thus, 18g toluene was added to 200g acid containing 50% BF₃ and 40% HNO₃ (98.6%). The mix was stirred vigorously during addition and maintained at 30–50° with cooling. The mixture was then refluxed (90–5°) for one hour, cooled to 70° and separated. The organic layer was poured into ice water and filtered. The residue was washed and dried. Some product was isolated similarly from the lower layer. The total yield of crude TNT, purity 65.6%, was 79.3%. Increasing the reflux time increased the yield and purity of the product. The spent acid was used to form DNT from toluene. The DNT was then nitrated in fresh acid to give TNT. This process eliminated the use of large quantities of H₂SO₄ in the manufacture of TNT.

A patent granted V. Vonasek claims an improved method of washing TNT and its mixts with DNT (Ref 83). Passing CO₂ thru the wash water prevents formation of brown side products and reduces the volume of washing liq. Thus TNT containing 30% dinitrotoluene of 0.1–0.5% total acidity (expressed as H₂SO₄) was fed at 85° at the top of a 1.20 liter washing column, while a 0.5–1% NaHCO₃ soln and 300 liter/hr of CO₂ were fed at the bottom. The product was pumped in a CO₂ atm into a 10 liter separator, H₂O was recycled and the product washed with H₂O in a 60 liter column with passing of CO₂ to an acidity of 0.001–0.0005% H₂SO₄. The earlier process without CO₂ yielded a dark-red to brown product of 0.03–0.05% acidity.

A three-step nitration process of toluene is described. The advantages of the modified process are reduced waste, less hazardous operation, reduced oleum requirement, partial replacement of concd HNO₃ with dil HNO₃, and higher rate of toluene flow into the reactor (Ref 86).

The continuous process of H.C. Prime (Ref 73) for preparing TNT was studied by thin-layer chromatography on silica gel with a starch binder and a fluorescent indicator. The nitration
products at various stages of nitration and the oxidation products from the nitration are identified. The purification process is improved by eliminating the use of soda ash and by lowering the pH (Ref 87).

TNT is claimed to be prep'd continuously from toluene by subsequent mono-, di-, and tri-nitration. Spent acid of the last step was passed thru the second step, extracted with O₂N₂C₆H₄Me (I) prep'd in the first step, and centrifuged to give (I), which was passed back into the second step, and spent acid which was recycled to the first step (Ref 88).

Miscellaneous Nitrations

Nakajima (Ref 71) gives a review of aromatic nitrations.

An app for continuous nitration of organic compds is described, comprising a circulation loop into which the organic compd, solvent, and nitrating agent are introduced continuously, with a heat exchanger for the desired reaction temp. Means are provided for recirculating the mixt, while withdrawing a portion into an acid separator and crystallizer. Nitration of 2,4-dinitromethyl-aniline with MA in dichloroethane solvent to give Tetryl is claimed (Ref 68).

The irreversible conversion of a primary aliphatic amine RNH₂ (R = Me, Me₂CH, Bu, EtMeCH, Me₂C₃, C₂H₂) (I, II, III, IV, V, VI) to its conjugate base with BuLi, subsequent nitration using EtONO₂ and acidification gave the corresponding nitramines, RN(NO₂)₂H (VII) (nitramine, solvent, % yield and bp/mm are given): I, Et₂O, 35, 80-5°C/10; II, 2:1 Et₂O-C₆H₄, 58, 87-8°C/10; III, C₆H₄, 49, 92°C/0.5; IV, C₆H₄, 45, 110°C/10; V, C₆H₄, 37, 86-7°C/10; VI, 2:1 Et₂O-C₆H₄, 46, -mp 38.0-0.8°C (C₆H₄)₄. Details of the procedure were given. The main disadvantage of the procedure is that amines bearing functional groups reactive with BuLi do not form nitramines (Ref 79).

A patent granted C.W. Plummer (Ref 84) describes the prep'n of polynitrohydrocarbons (I). These are saturated hydrocarbons having terminal polynitro groups, and may be prep'd by treating saturated hydrocarbons, having at least one terminal nitro group substituted in one terminal Me group, with tetratinmethane (II) in an alkaline soln of a base (NaOMe, NaOH, KOH, or NaHCO₃). Thus, to a chilled, stirred soln of 7.5g nitroethane in 150ml MeOH is added dropwise 77.5ml 2.58N methanolic NaOMe, and to the clear colorless soln (in an ice bath) is added 39.2g (II) at such a rate that the temp does not rise above 10°C. The orange soln is kept four days at room temp, the volume reduced to about 125ml in vacuo, and the residual soln poured into 400ml of water. Extraction of the colorless heavy oil with CH₂Cl₂ gives 7.7g crude orange liq, which distills at 34°C/1 mm to afford 6.80g colorless distillate, which crystallizes in the dry-ice chilled receiver. Most of the distillate liquefies at 10°C; the liq is decanted, and the solid is recrystallized from 2.5ml BuOH to yield 8.5% 1,1,1-trinitroethane (III), mp 53-5°C. The liq product (crude wt 5.4g, 45%) is mostly dinitroethane (IV). To a stirred and chilled soln containing 2.4g (V) and 14ml MeOH is added 4ml 0.02M NaOH and the resulting yellow soln (pH 8) stirred 15 minutes; 3.92g (II) is added rapidly, whereupon the color changes immediately to orange-red and the pH drops to ~7. The soln is kept at room temp 18 hours, after which the pH has dropped to about 5, then diluted with 200ml water and the turbid oil which separates is extracted with three 10ml portions CH₂Cl₂. The extract is washed with water, dried over Na₂SO₄, and the solvent removed at 20mm to give 2.7g yellow oil having a very strong odor of (II). The crude product is recrystallized from 2ml BuOH to afford 35% (III), mp 49-52°C. The following compounds are similarly prep'd (bp/mm, mp, d/temp, and RI/temp given): 1,1,1-trinitropropane, 23°C/2, 57.7°C, 1.3988/22°C, 1.4432/22°C, 1.1,1-trinitrobutane, -23°C, 1.3253/23°C, 1.4424/23°C, 2-methyl-1,1,1-trinitropropane, 33°C/0.35, 9.5, 1.3452/23°C, 1.4436/23°C, 1.1,1-trinitropentane, 50°C/0.7, -1.2740/25.5°C, 1.4443/25.5°C, 2,2-dimethyl-1,1,1-trinitropropane, -139-41°C, - - - 1,1,1-trinitrohexane, - (liq), - - - 1,1,1-trinitro-3-phenylnpropene, -35.5-36.5°C, - - - (I) are high expls which are much less sensitive than NG and may be used as substitutes for an equal amount of the latter in the manuf of blasting gelatins and Dynamites. When three parts by weight of these compds is absorbed in one part by weight of kieselguhr, Dynamites are produced which can be exploded by an engineer special blasting cap and fuse, and are superior to those made with NG because
they are less sensitive to shock, there is less danger of freezing, and they have a longer storage life. (I) may also be used in pure form for shooting oil wells, and because they contain large proportions of O and N are useful as ingredients in propellant compns, to increase the burning rate and gas volume. Incorporation of 30–40% by weight of (I) into NC produces a double-base propn of considerably improved power over that prep'd from guncotton alone. In addition, (I) are useful additives for hydrocarbon fuels to increase ignitability, and when mixed with Al may be employed as underwater expls.

Nitrohydrocarbons are produced by contacting atomized nitric acid with a molar excess of a hydrocarbon containing 1–10 C atoms in the gas phase in a reaction zone under superatmospheric press, and at a temp of at least 300° for a time ≈350 msec, and immediately quenching the resulting mixt to freeze the equilibrium of the reaction by expanding the reaction products thru an exhaust nozzle with simultaneous water cooling. A rocket engine with a reaction chamber, a fluid injection system for atomizing, mixing, and injecting fluids into the chamber, and an expansion nozzle, is a preferred reactor. Thus, a 35:1 mixt of CH₄ (natural gas) and HNO₃ (as 66% HNO₃) was heated 45msec at 571° and 150psig to give a 9.6% conversion to MeNO₂. Using a mole ratio of 11.6:1 at 510° and 150psig with a residence time of 225msec, a conversion of 10% was obtained (Ref 85).

Nitration of mononitrocarbanions, nitroform, and halonitromethane by nitryl fluoride is described by Fedorov et al (Ref 92). XC(NO₂)₂ and NH₄⁺C⁻(NO₂)₂X (X = NO₂; F, Br) were nitratd by FNO₂ to give the respective XC(NO₂)₂ in 39.1–90% yield. FNO₂ also converted C⁻HRNO₂ (R = Me, Et) and C⁻Me₂NO₂ to mixts containing AcOH and the corresponding RCH(NO₂)₂ and RC(NO₂)₂·NOH and Me₂C(NO₂)₂, Me₂C(NO₂)NO, and Me₂CO, respectively.

X. Safety in Nitrations

Since the nitrations of interest to us are exothermic reactions that produce expl substances it is obvious that safety is an important consideration in any laboratory nitration and even more so in an industrial nitration process. In the context of the discussion that follows, safety is taken to mean not only the accident-free production of expls but also the production of stable expls. Furthermore, some aspects of preventing pollution of the environment by nitration wastes will be included in this discussion.

The use of frictionless, spark-proof equipment and the necessity of good housekeeping in expl plants is too well-known to require further elaboration. Temp control during nitration has already been discussed in Sections V, VI, and VII. Here we will focus on potentially hazardous impurities formed during nitrations and on potential incompatibility of the nitration mixts with their surroundings and/or accidentally introduced impurities. We will confine our discussion to safety considerations in the manufacture of TNT and NG.

The manufacture of TNT is one of the safest operations in the explosive industry. Nevertheless, disregard of safety procedures may have disastrous consequences.

The most hazardous operations in TNT manufacture are the mononitration stages. In mononitration the hazard is due to the extremely violent reaction of the unreacted hydrocarbon with the MA, and to the fact that nitro derivatives of cresols are formed in the process, along with nitrotoluenes. The last stage — tri-nitration — is dangerous due to the drastic conditions of the reaction which requires concd acids and a high temp. The earlier method of tri-nitration at which temps up to 120° were applied was particularly hazardous. If the mononitrotoluene has not been freed from nitrocresols, tri-nitration is still more dangerous, due to the high reactivity of nitrocresols, and their liability to undergo oxidation.

According to Urbanski (Ref 74, p 391): "The spent acid from tri-nitration has also been the cause of several disasters, although it had been considered safe to handle. The most noteworthy example of this occurred in the Reinsdorf factory in Germany in 1935. The hot spent acid flowed down to open iron tanks, where, as the liquid cooled, a mixture of di- and tri-nitrotoluenes rose to the surface. It was skimm'd off from time to time and transferred to a washing tank, where it was washed with water. On skimming, a rubber glove and a shelf left on the rim of the tank with some
cotton wool on it, fell into the tank. The re-
action between the spent acid and the rubber
and cotton wool initiated violent decomposition
and fire. An attempt to extinguish the flames
failed, and soon the nitro compounds on the
surface of the spent acid exploded. The explo-
sion and fire spread over several nearby tanks,
then to the nitro compounds in the washing tank.
As a result the whole plant for the recovery of
nitro compounds was destroyed. In addition to this
the expl tore away the roofs of some nearby
buildings, among them drier buildings located
at a distance of about 660m. Parts of the tank
thrown off by the explosion into one of the
driers detonated the TNT present, and in another
they caused the ignition of the load. Similar
explosions or fires spread over further buildings
of the TNT factory. Moreover, a neighboring
nitroglycerine plant also exploded. This dis-
astrous explosion cost 82 human lives and in
addition 104 people were seriously and 700
lightly injured.”

It is known that alkalis react with TNT to
form sensitive expls. Urbański (Ref 74, p 392)
gives an example of a disastrous accidental
exlpn in a French TNT plant which could have
resulted from the interaction of TNT and alka-
line Na carbonate: “Investigations showed that
the explosion occurred after about 2000kg of
TNT in a drying tank had caught fire. The TNT
in question was that recovered from the spent
acid from trinitration. It is known that such a
product contains various impurities, among them
the isomers of α-trinitrotoluene, nitrocresols,
etc. It had first been washed with water at 90°C,
then with a 6% solution of Na carbonate, and
again with water. The drying was effected at
85–90°C by passing air for 8 hours. In the case
described, as the drying TNT still contained
some acid, 7kg of Na carbonate (ie, 0.35% in
relation to TNT weight) were added to the tank
with the drying TNT which at the time contained
only a very small quantity of water. This must
have led to the formation of typical decomposi-
tion products of TNT brought about by reaction
with alkalis. It is highly probable that these
compounds were the first to ignite, whereupon
the flames spread over the whole drier”

Kovache & Thibon (Ref 10) describe a num-
ber of expls that occurred in French TNT
plants during 1917–18. These were ascribed to
the formation of reaction products of TNT with
lead or iron in the presence of dil nitric acid.
These products were found to be very sensi-
tive to impact, friction, and contact with coned
acids. Such products were found at the expln
sites.

The most recent major expln in a US TNT
plant occurred in May 1974 at the Radford
Army Ammunition Plant. The accident com-
pletely destroyed one of the three continuous
nitrations lines at the plant. According to the
AMC News, Sept 1974, the investigation board
reported that an operator inadvertently intro-
duced a 5 to 6-foot rubber hose “to clean out
unwanted material that had collected in a trans-
fer line leading to the nitrator, when the hose
was pulled from his hands into the nitrator.
This resulted in a rapid temp rise and subsequent
explosion. The hose was commonly used in this
manner”. The material causing the blockage in
the transfer line was believed to be an oxidation
product of TNT, 2,2′-dicarboxy-3,3′,5,5′-tetra-
nitroaoxybenzene, also referred to as White
Compound. The introduction of the rubber
hose caused a rapid, exothermic oxidation re-
action between the hose material and the mixed
acid present. The heat generated by this re-
action caused a local acceleration of the normal
nitrations/oxidation reactions which occur in the
nitrator until a critical temp was reached, at
which point rapid oxidation of DNT/TNT pro-
cceeded as a runaway reaction, igniting the ma-
terial present in the vessel.

According to the AMC News article “authori-
ties summed up the report by pointing out that
the incident was not the direct result of normal
operations, but rather was the result of an un-
usual condition, and that the design and op-
erating procedures were not unsafe when con-
sidered in the context of the total hazardous
environment. The process in the nitration and
purification building was operating normally
when the rubber hose was introduced into the
system.

In all, the board submitted 32 recommenda-
tions as a result of its investigation. They in-
clude additional training for personnel in nitra-
tion and purification areas to enable them to
cope with such emergency situations. The board
also recommended the development of sensing
equipment to uncover possible hazardous condi-
tions earlier in the TNT manufacturing process”. 
Although damage to the plant was extensive, there was no loss of life. There were 15 disabling and 102 non-disabling injuries. Slight damage and minor injuries also resulted beyond the plant boundary from the blast and flying debris.

NG, unlike TNT, can become very unstable on prolonged contact with acid. Explos of NG in contact with spent acid have occurred. Studies by Oehman et al (Ref 56) have demonstrated which spent acid compnns are "safe" and which are dangerous in contact with NG or EGDN. Their results are summarized in Fig 28.

![Safety diagram of acidic nitroglycerine, according to Oehman et al (Ref 56). For comparison, nitroglycerol is also indicated.](image)

Accidents have also occurred while NG was being transported around manufacturing facilities via gravity flow in gutters. To increase the safety of such transport, "detonation breakers" can be introduced along its flow path. An example of a detonation breaker is shown in Fig 29 which consists of a lead tank half-filled with water. NG flows into the tank, collects on the bottom and runs on from below thru the siphon. This arrangement interrupts the NG stream. Detonation cannot be transferred readily thru the water barrier.

Further increase in safety can be achieved by flowing NG as water emulsions. These should consist of no less than 3 parts of water per part of NG, since 1:5:1 or even 2:1 emulsions can be detonated (Ref 41).

Some recent publications on nitration safety are listed below:

- S. Raczyński, Przemysł Chem 42(9), 470 (1963) & CA 59, 15114 (1963) (A discussion of technological difficulties in attempting to reduce explosion hazards during nitration)
- S. V. Egorov et al, Otkrytiya, Izobret, Prom Obraztsy, Tovaryne Znaiki 46 (34), 199 (1969) & CA 72, 91696 (1970) (Describes an automatic safety system for nitration processes based on the generation of warning signals by press inside the nitratior)
- L. Albright & C. Hanson, Loss Prevention 3, 26 (1969) & CA 72, 99685 (1970) (Kinetics and mechanism of aromatic nitration are reviewed in terms of safety considerations)
- T. A. Ventrone, Ibid 38 & CA 72, 113375 (1970) (A number of explosions during batch nitration are described. The effects of temp, rate of addition, and ratio of reactant on the explns are shown. It is suggested that safety standards be determined and enforced)
- E. J. Fritz, Ibid 41 & CA 72, 113380 (1970) (A detailed investigation was made of a nitration expln, including lab simulation of the event. The expln took place in production of dinitrobenzene in a batch nitratior. The problems of avoiding this sort of expln are detailed)

An interesting survey of pollution abatement in munition plants was recently published by I. Forsten of PicArsn (Ref 91). This article...
focuses on pollution abatement in TNT manufacture and describes air pollution and water pollution as separate facets of the overall pollution problem. Air pollutants in TNT production are primarily oxides of nitrogen, MNT and TeNMe. The main water-pollutant is "red water" produced during the Na₂SO₄ (sellite) purification of TNT. To a lesser degree "Pink water" is also a problem in munition loading plants. This is formed during washing of TNT loading bays, particularly when the wash waters are of elevated pH and the TNT dissolved in them undergoes photochemical reaction.

Air pollutant control is still in the pilot plant stage. Two methods appear promising for controlling oxides of nitrogen. These are molecular sieve absorption and acid scrubbing. Both are described in the Forsten article. Scrubbing with sellite is being evaluated as a means of removing TeNMe from the exhaust gases.

Water pollution can be mitigated by aeration of the wash streams formed in the sellite treatment of TNT. Further control can be achieved by incineration of the "red water". However, the oxides of nitrogen and the Na₂SO₄ ash thus formed can be troublesome. A recently developed scheme of converting this ash to Na₂CO₃ and H₂S, which can then be recycled to form sellite, looks promising.

Activated carbon can be used to preclude the formation of "pink water". Methods of reactivating the carbon are still under investigation.

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Nitrato. Prefix indicating an organic compound containing the radical –O.NO₂

Nitratodimercuriacetaldehyde.
OHC(C₃H₅).Hg.O.NO₂, mw 504.20, N 2.77%, colorless powd., prills off on heating, practically insol in w. Can be prp'd by passing acetylene, or by the gradual addition of an alc soln of acetaldehyde, into a soln of mercuric nitrate in dil nitric acid

Refs: 1) Beil 3, 606 (listed under Oxidimercuroacetaldehyde) 2) K.A. Hofmann, Ber 31, 2213 & 2784 (1898) and 38, 2002 (1905)

Nitratothimercuriacetaldehyde.
OHC(C₃H₅).Hg(O₉).Hg.O.NO₂, mw 720.79, N 1.94%, light grey powd., prills off on heating. Can be prp'd by passing a stream of acetylene for 2 hrs thru a mercuric oxide soln in 30% nitric acid

Refs: 1) Beil 3, 607 2) K.A. Hofmann, Ber 31, 2787 (1898) and 38, 2004 (1905)

NITRATOPHOSPHITES

Several salts of a hypothetical nitratophosphorous acid, H₅N₃H₂P₂O₇, are known which are explosive

Lead Nitratophosphate (LNP).
Pb(NO₃)₂.Pb(H₂P₂O₇)₂ or [Pb(NO₃)(H₂P₂O₇)], mw 668.43, N 4.19%, heavy white granular crystals; mp, starts to decomp above 100°, prills off at about 180°C. Was prp'd by von Herz (Ref 2) by adding a hot satd soln of Pb nitrate (331g) to a boiling satd soln of Ca hypophosphite (170g), cooling the mixt rapidly with efficient stirring, upon which Pb hypophosphite separates. After filtering, 250g of the ppt are added with stirring to a boiling soln of Pb nitrate (500g) in 1500mL of w, and rapidly cooled. The LNP ppt is filtered and dried at 40–50°C. Its rate of deton is comparable to that of LA and its thermal stability is quite good (no weight loss at 80°C for several days). It burns in air, producing a hot flame.

The relatively small volume of gas liberated on its decomp. [2 Pb(NO₃)₂.Pb(H₂P₂O₇)₂ → 2Pb₂P₂O₇ + 4H₂O + 2N₂ + O₂ (117k/ks, as contrasted with 314k/ks for MF or 230k/ks for LA), inhibits its use as an initial expl by itself, but does not prevent its use in mixts such as LNP 30–60%, Sb sulfide & Ba nitrate, 70–40%.

Its suitable sensitivity to friction and impact (comparable to that of MF), its stability and high flame temp, render it very suitable for percussion-fuze use. An additional asset is that LNP functions in a practically smokeless manner, leaving little residue or slag


Mercurous Nitratophosphate.
HgNO₃.Hg(H₂P₂O₇).H₂O, mw 546.24, N 2.56%, white powd.; mp, turns grey at 90°C, explds at 100°C. It was prp'd by Hada (Ref 2) by adding a fairly concd soln of K hypophosphite to a
soln of mercurous nitrate, avoiding an excess of hypophosphite. [The soln of mercurous nitrate, free from nitrous acid, can be prepared by dissolving mercuric oxide to saturation in nitric acid, and then shaking the soln violently with metallic Hg for a few minutes.] As the Mercurous Nitratophosphite ppt decomp when left in contact with the mother liquor, it must be filtered and dried immediately on a porous plate without washing. It is si sol in w, in which it decomp with the separation of Hg.

Mercurous Nitratophosphite expids on being heated to about 100°, or on being touched with a hot wire. When left in a vacuum desiccator, it eventually loses its w of crystn, but undergoes no decopmp

Refs: 1) Mellor B (1928), 885 2) S. Hada, JCS 67, 225 (1895)

Nitre. Same as Saltpeter. See as K nitrate under List of Nitrate Compounds in this Vol.

Nitratrerythrite. Fr for Erythritol Tetranitrate. See in Vol B, E124-L to E125-L.

**NITRIC ACID**

HNO₃, mw 63.02, N 22.23%, colorless liq when free of dissolved NO₂, otherwise si yel. Possesses a pungent odor; vapors toxic when inhaled. Mp −41 to −42°; bp 86° (decomp, 21.5° at 24mm, d 1.502g/cc at 25/4°, RI 1.397 at 16.4°. Sol in eth & w. The following varieties are commercially available in the USA:

1) Nitric acid c.p., d 1.42g/cc, which corresponds to about 70% HNO₃
2) Nitric acid, tech 40°Be, which corresponds to about 62% HNO₃
3) Nitric acid, c.p., Fuming, d 1.50g/cc, which corresponds to about 95% HNO₃
4) Nitric acid, tech, “Fuming”, d 1.49−1.50 g/cc, which corresponds to 90% HNO₃
5) Nitric acid, c.p., “Red Fuming”, d 1.59−1.60g/cc, which corresponds to 100% HNO₃ containing about 25% dissolved NO₂
6) Nitric acid, tech, “Red Fuming”, d 1.59−1.60g/cc — same as above

7) Nitric acid, c.p. absolute (100% HNO₃), d about 1.513g/cc (Refs 33, 34, 37, 39 & 40)

**Historical.** A deposit of metallic Ag as part of the markings on ancient Egyptian mummy cases has led to the conclusion that since Ag nitrate was used to form these markings, a knowledge of the manuf & use of nitric acid to prepare the Ag nitrate must certainly have been available (Ref 30). However, the first written description of the prepn of nitric acid, known as “aqua dissolutiva”, appeared in the 17th century Latin work, “De Inventione Veritatis”, wherein it was claimed that the method was discovered by the Arabian alchemist Geber in the 8th century (Refs 9, 13 & 30). The described acid was capable of dissolving Ag or S, and, when mixed with sal-ammoniac, of dissolving Au. The method of prepn consisted of distg saltpeter with vitriol, perhaps in the form of sulfates such as those of Cu, and Al. A similar method was used by Albert Magnus in the 12th century, whereas the Frenchman R. Lully (Lullins), in the 13th century, heated saltpeter with either Fe sulfate or clay. G. Agricola, in the 16th century, described all the previous methods employed, and J. Kunckel, in the 17th century, prepared it by heating saltpeter with white As. In the same century (about 1648), J.R. Glauber prepared nitric acid by heating saltpeter with sulfuric acid, a method that was used thereafter until recently replaced by the ammonium oxidation method. Glauber proved that his product was the same as the acids previously obtained by heating saltpeter with substances other than sulfuric acid. He called his acid “aqua fortis” & “spiritus acidus nitri”, but it later became known as “spiritus nitri humans Glauberi”. The French at first called it “eau de depart”, then “l’esprit de nitre” & finally “l’acide nitrique” or “l’acide ayotie”. The Germans at first called it “scheidwasser” (by Basil Valentinus in 1624) & later, “stickstoffsaure”

In about 1750, a Frenchman, G.F. Rouelle, devised a method for concg the acid by distg the weak nitric acid with concd sulfuric acid. This method is used even at the present time (Ref 30)

The chemical nature of the acid remained unknown for a long time, further investigation being obscured thruout the late 17th & early
18th century by the Phlogiston Theory. In 1776, A.L. Lavoisier demonstrated the presence of oxygen in nitric acid, and in 1785, H Cavendish showed that nitric acid was produced when humid air was submitted to electric sparking, conclusively proving it contained both nitrogen & oxygen. In 1816, J.L. Gay-Lussac & C.L. Berthelot established its exact compn (Ref 30).

The application of nitric acid to the arts & crafts seems to have followed shortly after sulfuric acid became an article of commerce. With the invention of the distn process by Glauber in 1648, the acid seems to have been in demand by jewellers, gilders & brass-finishers, because of its effect on most of the non-ferrous metals, especially Cu. It was used for the "parting" of Au from Ag and for Au & Pt refining. However, for centuries the principal object for the collection or manufacture of nitric acid has been the prepn of gunpowder, expls & proprials (Ref 30).

Nitric acid occurs naturally, in traces, in the atmosphere & in rain w from the electrical discharge of lightning and from nuclear expls. Indeed, the natural nitrates of the world have probably been formed by the action of naturally occurring nitric acid to the extent of 4–6 lbs of combined nitrogen per acre (Ref 30).

For many years nitric acid was prep by the method of Glauber which involves heating saltpeter with concd sulfuric acid. In 1798, I. Milner experimentally oxidized NH₃ vapor over heated Mn dioxide; the resulting nitric acid fumes were led into w. In 1824, W. Henry almost duplicated the present commercial method of manuf when he showed that ammonia could be oxygen oxidized in the presence of a Pt sponge catalyst. Until 1900, commercial prodn of nitric acid used K nitrate & sulfuric acid. However, with the opening of Chilean saltpeter deposits, K nitrate was replaced by Na nitrate. Birkeland & Eyde developed their electric arc process in Norway in 1903, replacing the distn process. In 1908 the first commercial ammonia oxidation plant was built in Germany with a 3-ton per day capacity. An economical source of NH₃ was assured with the development of the Haber-Bosch ammonia synthesis process in 1913. The very heavy demands for electrical power made the electric arc process economically unfeasible when compared with the NH₃ oxidation process (Refs 30, 34 & 36).

Uses. Since 1947, 70 to 85% of the annual USA production of nitric acid has gone into the production of NH₄ nitrate fertilizer, initially in the form of solid prills; currently, increasing amounts have been supplied mixed with excess ammonia and/or urea as aqueous "nitrogen solution" for direct application to the soil. Some 15% is used in expls (nitrates & nitro compds), and about 10% is consumed by the chemical industry. As the red fuming acid or as nitrogen tetroxide, nitric acid is used extensively as the oxidizer in propiels for rocketry. It is estimated that current USA capacity for nitric acid is in excess of 10 million tons (Refs 30, 34, 36 & 37).

Processes for Nitric Acid Manufacture.

All processes for the manuf of concd nitric acid have the following stages in common:

(a) Formation of nitric oxide, NO
(b) Oxidation of nitric oxide to nitrogen peroxide, which is a mixt of NO₂ and N₂O₅
(c) Absorption of peroxide in w to form a weak soln of nitric acid
(d) Concentration of the weak acid to the required grade of acid

There is only one exception to this scheme, a process in which highly concd nitric acid is directly produced by absorption of the nitrogen oxides in perchloric acid (Ref 36).

Nitric Acid from Saltpeter. In the manuf of nitric acid from Chilean saltpeter, 85 parts of saltpeter and 98 parts of concd sulfuric acid (both calculated on 100% basis) were heated together in large iron retorts, often capable of holding 5 tons or more of ingredients. The following reaction took place:

\[ \text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{HNO}_3 + \text{NaHSO}_4 \]

The reaction should be conducted below 150° to avoid loss by decomp of the HNO₃. The resulting "bisulfate" residue is obtained in an easily fusible mass, which could be withdrawn in a fluid condition merely by opening a plug at the bottom of the retort. However, in actual practice, it was preferred to raise the temp toward the end of the reaction so that part of the w would be driven off: 2NaHSO₄ = Na₂S₂O₇ + H₂O. The resulting pyrosulfate was run off in a fluid condition into iron pans, where it solidified and was called "nitre cake". This cake could be con-
verted either into Na₂SO₄, by heating with NaCl, or into Na₂S (Refs 7, 8, 9, 12, 16 & 30). If weak nitric acid is distilled without being previously mixed with sulfuric acid, the highest concn obtainable in the distillate is about 68%, because nitric acid forms a constant boiling mixt with w at that concn.

In addition to systems using distn at atm press in the prepn of nitric acid, there was also the so-called Valentinier's Vacuum Process. This method was more expensive to install, but it gave whiter acid because distn was conducted at low temp, thus avoiding decompn of HNO₃ with consequent formation of NO and NO₂. The Valentinier process was modified so as to obtain the best results with the press reduced to 15–25 mm of Hg.

A continuous process for the manuf of nitric acid from saltpeter and sulfuric acid was introduced in 1894 by Prentice (Ref 9, p 147). *Nitric Acid by the Oxidation of Ammonia.* Here, the catalytic oxidation of ammonia under press using a Pt catalyst maintained at a temp of 900–1000° is the process used. The reaction press is the rate determining step, being directly proportional to the product nitric acid concn (Refs 6, 22, 26, 30, 34, 36, 37 & 41).

*Direct Production of Concentrated Nitric Acid.* The concept of "direct production" of nitric acid covers many processes. In one, q nitrogenic acid is agitated with an excess of liq nitrogen dioxide (N₂O₄) until two layers are formed. The lower layer consists of a soln of N₂O₄ in nitric acid of about 75% strength, while the upper layer consists of liq N₂O₄ in which is dissolved strong (98–99%) nitric acid. The upper layer is removed and the N₂O₄ driven off by distn.

Manning (Refs 18 & 19) describes a method of direct prepn of strong nitric acid in which a mixt of dil (60–65%) nitric acid and liq N₂O₄ is treated with oxygen under high press.

Atroschenko and Kargin (Ref 26, pp 223–268) describes several methods of prepn of concd nitric acid directly from oxides of nitrogen.

Instead of using air for the oxidation of ammonia, some investigators, for instance Cze and Chi Wu (Ref 21), advise using oxygen, especially in cases where oxygen is available cheaply. According to Thorpe (Ref 22, p 571), the use of oxygen was first recommended by Partington and Prince in 1924.

Many variations in nitric acid processes are operated, and are distinguished by the characteristic conditions of the oxidation of ammonia and absorption of the oxides to produce nitric acid, and by the concn or strength of the nitric acid which is produced. These processes are known by such titles as atmospheric process, pressure process, Montecatini process, Bamag-Meguin process, etc. Pressure process plants are those in which both oxidation of ammonia and absorption of oxides are carried out under superatmospheric press, generally in the range of 50 to 125 psig. These plants comprise over 62% of the installed capacity of the USA (Ref 36). Most of these plants as well as pressure process plants constructed more recently, produce nitric acid of a concn not greater than about 62% and generally in the range of about 50 to 60% strength. In recent years, considerable progress has been made in increasing the size and in proving both the thermal and the economic efficiency of pressure process nitric acid plants, so that plants of recent construction are thermally self-sufficient; on balance they may even be net producers of energy, usually in the form of steam, which can be utilized in other nearby operations outside the nitric acid manuf plant. But the standard product of these more economical, larger, modern, thermally self-sufficient, pressure process nitric acid plants has continued to be nitric acid of strengths up to but not exceeding about 62% concentration, by wt (Ref 36).

Much nitric acid is used at concns of 95% by weight, or more. Acids of this concn can be produced directly by more costly processes, but generally are produced most economically by a separate nitric acid concentrating operation on feed of dil nitric acid from a pressure nitric acid plant. Such concn requires extractive distn of weak nitric acid in the presence of a third component, such as sulfuric acid or magnesium nitrate, which acts as a dehydrating agent. Obviously, less of the dehydrating agent will be required if the nitric acid feed to the process is stronger than 63% by weight (Ref 36).

Absorption of Nitrogen Oxides in Water to Form Nitric Acid Solution. The production of nitric acid from nitrous gases such as are obtained in
the catalytic combustion of ammonia, requires an oxidation of these gases and their absorption in w or an ac soln already containing nitrogen oxides. In this process, the nitric oxide has to be converted into nitrogen dioxide. By absorption of the nitrogen dioxide in w, nitric oxide is formed, besides the nitric acid, and this nitric oxide has to be subjected once more to oxidation. In the large scale manuf of nitric acid, the oxidation and absorption of the nitrous gases has hitherto been carried out in acid towers or columns, in which the absorbing liq, which is w or a dil acid soln, starting at the top of the tower, uniformly trickles thru several layers of packing material, being collected at the bottom of the tower in a collecting vessel, from which it is lifted by a pump, after having been duly cooled, back to the top of the tower (Ref 36)

*Nitric Acid Production in a Nuclear Reactor.*

While this process is widely applicable, it has been found to be highly advantageous in the fixation of nitrogen. Thus, it is possible to directly produce nitrogen dioxide from the normal constituents of air thru the utilization of the energy of recoil fragments from atomic fission. One possible highly useful product of such a reaction is nitric acid, which can be processed from nitrogen dioxide by the addition of w and oxygen after sepn of the nitrogen dioxide from unreacted gases and admixed radioactive fragments. Particularly advantages of this process include the following: the only raw materials required are air and w; a low operating temp is combined with a high effective processing temp; the process has an inherent ultrafast built-in quench; and the process achieves the direct conversion of nuclear energy into chemical energy (Refs 34 & 36)

*Nitric Acid Production by Detonation Incurred Shock Wave.* J.F. Haller (Ref 36) found that passing a detonation or shock wave thru a gaseous mixt comprising nitrogen and oxygen produces nitrogen oxides. According to this process, a make charge of a gaseous mixt comprising nitrogen and oxygen is introduced into a portion of a reaction space, and a detonatable material is introduced into the remaining portion. The detonatable material is detonated and the detonation wave impinges on the make charge, causing reaction between the nitrogen and oxygen and formation of nitrogen oxides.

The nitrogen oxides produced are suitable for use in making the corresponding acids

*Nitric Acid Production using Pebble Bed Regenerators (Wisconsin Thermal Process).* When air or similar mixts of nitrogen and oxygen are subjected to temps of the order of 2000°C, part of the nitrogen and oxygen react with one another to form nitric oxide, this reaction being generally termed "nitrogen fixation". The reaction is reversible, however, and the newly formed nitric oxide will quickly decomp into its constituents, unless the temp is rapidly reduced to materially lower levels at and below which the rate of decomp is so slow as to be negligible. Thus, to recover nitric oxide for practical use, the reaction gases must be rapidly chilled to a sufficiently low temp to stabilize the nitric oxides.

In his US Patent 2422081, Frederick G. Cottrell (Ref 36) discloses methods and apparatus to meet this requirement while at the same time providing such rapid chilling rates for the newly formed nitric oxide as will reduce its decomp to a tolerable minimum. According to this patent, the hot reaction gases produced in the combustion zone of a furnace are passed thru a bed of heat-absorbing pebbles of a refractory material that chill the bases and are themselves heated in the process; after the pebbles in the bed have become heated to a sufficiently high extant, the direction of the process is reversed; that is, the fresh air is delivered to the combustion zone thru the newly heated pebble bed, while the reaction gases are discharged thru another pebble bed located at the opposite side of the combustion zone (Ref 36). The process is not considered to be economically feasible (Ref 34)

*Laboratory Preparation of Absolute Nitric Acid.* Strong nitric acid, 99%, free from oxides (white) is used for many nitrations. Since nitric acid of this quality is not generally commercially available, it is usually prepd in small quantities in the laboratory as needed. The customary procedure is to mix one p of concd nitric acid (d 1.42g/cc) with 2p of sulfuric acid (d 1.84g/cc) and to distill the nitric acid from this mixt under reduced press, using an all glass system.

Distillation under reduced press is necessary to minimize the decompn of pure nitric acid,
which decomp while being distd according to the equation: 4HNO₃→2NO₂+2H₂O+O₂ (Refs 13 & 32)

The vacuum distn of a mix of Na nitrate and concd sulfuric acid, with condensation of the liq just above its fr p, results in a colorless liq with a fr p of −41.5⁰ (Refs 32 & 34)

**Properties of Nitric Acid**

*Physical Properties.* According to Lagowski (Ref 32), X-ray analysis of a single crystal of nitric acid shows a monoclinic unit cell (symmetry P2₁/a−C₂/n) with the following dimensions: a=16.23, b=8.57, and c=6.31Å, and β=90⁰. The unit cell contains 16 molecules, and the calc d is 1.895g/cc at −41.6⁰.

The Raman spectrum of the monohydrate, HNO₃·H₂O, shows it to exist as the hydroxoniun salt, H₂O⁺NO₃⁻. Also, according to analyses of the Raman spectrum, nitric acid exists in aq solns either as a pseudo-acid, NO₂·OH or as a true acid, NO₃⁻·H⁺. In 10 molar aq soln, both acids are present in equal amounts, being caused by the self-dissociation of nitrogen pentaoxide (N₂O₅), while in a 6 molar soln, the pseudo acid is present only to the extent of 2%, and the more dilute the soln, the less pseudo acid is present. In very concd solns, the true acid is present only in small quantities (Refs 32 & 33).

The liq acid has a mw greater than that expressed by the formula HNO₃, probably H₂N₂O₄ or H₃N₃O₅.

Pure abs nitric acid exists only below its fr p as a white crystalline mass. The moment it becomes liq, some slight decomp occurs and the acid assumes a light coloration due to the formation of nitrogen dioxide.

The nitrate ion (NO₃⁻) is one of the most electronegative ions and its absolute velocity at 18⁰ under a potential gradient of 1 volt per cm is 6.4 x 10⁻⁴ cm per second (Ref 9, p 340).

It can be seen from Fig 1 (Ref 30, p 13), that when an aq soln of nitric acid is boiled under atm press, mostly w at first evaporates with only a small amount of HNO₃. This lasts until the concn of the distillate reaches 68.18% HNO₃ and the bp climbs to 121.70⁰. Further boiling would neither increase nor decrease the concn of the distillate and it may be said that the 68.18% acid is a constant boiling mixt. If the press is reduced to 735mm, the bp drops to 120.5⁰ and the compn of the distillate is reduced to 68% HNO₃.

According to Kirk & Othmer (Ref 34), nitric acid is completely miscible w and is generally known and used as an aq soln, sometimes with the addition of dissolved nitrogen oxides at high concns. Two hydrates may be crystallized from aq solns: a monohydrate (HNO₃·H₂O), corresponding to 77.77% acid by wt, and a trihydrate (HNO₃·3H₂O), corresponding to 53.83% by wt, melting at −18.48⁰. With local maxima at the freezing points of the four crystal forms, the freezing point curve for nitric acid solns is quite irregular. Local minima are found at concns of about 32, 71, and 91% acid, as shown in Table 1 (Ref 34, p 798).

The heat capacities of liq & gaseous nitric acid may be expressed as functions of the absolute temp, T, by Eqs 1 & 2 (according to Lagowski, Ref 32, p 153)

\[
\begin{align*}
\text{Cp (liq)} &= 28.64\,(8\times10^{-3}\,\text{T}), \\
T &= 232−305\,^\circ\text{K} \\
\text{Cp (gas)} &= 6.57\,(18.75\times10^{-3}\,\text{T}), \\
T &= 275−500\,^\circ\text{K} 
\end{align*}
\]
### Table 1
Physical Properties of Nitric Acid Solutions

<table>
<thead>
<tr>
<th>Percent HNO₃ by wt</th>
<th>Density at 20°C, g/ml</th>
<th>Freezing point, °C</th>
<th>Boiling point, °C</th>
<th>Specific heat at 20°C, cal/(g)(°C)</th>
<th>Partial pressures at 20°C, mm Hg</th>
<th>Viscosity at 20°C, cP</th>
<th>Thermal conductivity at 20°C, Btu/(hr)(ft²)(°F/ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.99823</td>
<td>0</td>
<td>100.0</td>
<td>1.00</td>
<td>17.5</td>
<td>1.0</td>
<td>0.35</td>
</tr>
<tr>
<td>10.0</td>
<td>1.0543</td>
<td>-7</td>
<td>101.2</td>
<td>0.89</td>
<td>17.0</td>
<td>1.1</td>
<td>0.33</td>
</tr>
<tr>
<td>20.0</td>
<td>1.1150</td>
<td>-17</td>
<td>103.4</td>
<td>0.81</td>
<td>15.2</td>
<td>1.2</td>
<td>0.31</td>
</tr>
<tr>
<td>30.0</td>
<td>1.1800</td>
<td>-36</td>
<td>107.0</td>
<td>0.76</td>
<td>13.2</td>
<td>1.4</td>
<td>0.29</td>
</tr>
<tr>
<td>40.0</td>
<td>1.2463</td>
<td>-30</td>
<td>112.0</td>
<td>0.72</td>
<td>10.8</td>
<td>1.6</td>
<td>0.27</td>
</tr>
<tr>
<td>50.0</td>
<td>1.3100</td>
<td>-20</td>
<td>116.4</td>
<td>0.68</td>
<td>7.9</td>
<td>1.9</td>
<td>0.25</td>
</tr>
<tr>
<td>60.0</td>
<td>1.3667</td>
<td>-22</td>
<td>120.4</td>
<td>0.63</td>
<td>4.9</td>
<td>2.0</td>
<td>0.23</td>
</tr>
<tr>
<td>70.0</td>
<td>1.4134</td>
<td>-41</td>
<td>121.6</td>
<td>0.58</td>
<td>2.9</td>
<td>2.6</td>
<td>2.0</td>
</tr>
<tr>
<td>80.0</td>
<td>1.4521</td>
<td>-39</td>
<td>116.6</td>
<td>0.53</td>
<td>10.5</td>
<td>0.9</td>
<td>1.9</td>
</tr>
<tr>
<td>90.0</td>
<td>1.4826</td>
<td>-60</td>
<td>102.0</td>
<td>0.47</td>
<td>27.0</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>100.0</td>
<td>1.5129</td>
<td>-42</td>
<td>86.0</td>
<td>0.42</td>
<td>45</td>
<td>0.9</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The thermodynamic properties of nitric acid and its hydrates are given in Table 2 (Refs 32 & 34)

### Table 2
Thermodynamic Properties of Nitric Acid and Its Hydrates

<table>
<thead>
<tr>
<th></th>
<th>HNO₃</th>
<th>HNO₃·H₂O</th>
<th>HNO₃·3H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitric acid, wt %</td>
<td>100.0</td>
<td>77.77</td>
<td>53.83</td>
</tr>
<tr>
<td>freezing point, °C</td>
<td>-41.59</td>
<td>-37.62</td>
<td>-18.47</td>
</tr>
<tr>
<td>heat of formation at 25°C, kcal/mole</td>
<td>-41.404</td>
<td>-112.966</td>
<td>-212.203</td>
</tr>
<tr>
<td>free energy of formation at 25°C, kcal/mole</td>
<td>-19.100</td>
<td>-78.410</td>
<td>-193.701</td>
</tr>
<tr>
<td>entropy at 25°C, kcal/(mole)(°K)</td>
<td>37.19</td>
<td>51.83</td>
<td>82.92</td>
</tr>
<tr>
<td>heat of fusion, kcal/mole</td>
<td>2.503</td>
<td>4.184</td>
<td>6.954</td>
</tr>
<tr>
<td>heat of vaporization at 20°C, kcal/mole</td>
<td>9.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat of dilution to infinite dilution, kcal/mole</td>
<td>-7.97</td>
<td>-4.73</td>
<td>-2.12</td>
</tr>
<tr>
<td>gaseous entropy, cal/mole (°K)</td>
<td>63.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The thermodynamics for aq dilution of nitric acid is expressed by Eq 3 and the heat of dilution can be found in Fig 2 (Ref 30, p 15)

\[
\text{HNO}_3 (\text{liq}) + x\text{H}_2 \rightleftharpoons \text{HNO}_3 \cdot x\text{H}_2\text{O(s)}
\]

\[
\Delta G^\circ = -2523 -4404
\]

(cal/mole)
The equilibrium constant, $K_p$, varies with temperature in the following manner:

$$T^\circ, K \quad 343 \quad 363 \quad 391 \quad 393$$

$$\log_e K_p \quad 4.6 \quad 2.9 \quad 0.25 \quad 0.15$$

The values for surface tension, $\gamma$, are (Ref 32):

$$t, ^\circ C \quad 0 \quad 20 \quad 25$$

$$\gamma, \text{dynes/cm} \quad 43.56 \quad 41.15 \quad 40.00$$

The equation for the free energy of vaporization of nitric acid for the temp range 275–305$^\circ$K has been obtained from vapor pressure measurements (Ref 30):

$$\Delta G = 14744 + 22.07T(\log_e T) - 13.38 \times 10^3 T^2 - 166.26T$$

(cal/mole) \hspace{1cm} (6)

The bp calcs using Eq 6 is 84$^\circ$C.

The electrical properties of nitric acid are presented in Table 3 (Ref 30):

**Chemical Properties**

The action of nitric acid on various metals as well as on construction materials is described in Perry's Handbook, 3rd ed (Ref 28, p 1502); in the book by Atroschenko and Kargin (Ref 26), pp 366–369 and in Refs 23, 24 & 25.

According to Kirk & Othmer (Ref 34), the reactions of nitric acid may be classified conveniently into three groups: (1) reactions as an acid (formation of inorganic nitrates); (2) reactions as an oxidizing agent; and (3) organic reactions.

Nitric acid is a strong, monobasic acid. It reacts readily with alcalines, oxides, and basic materials, forming salts. The reaction with ammonia, forming ammonium nitrate, for use as a fertilizer, is by far the largest single industrial outlet for nitric acid.

Nitric acid is a strong oxidant. Organic materials such as turpentine, charcoal, & charred sawdust are violently oxidized, while alc may

---

### Table 3

Electrical Properties of Nitric Acid

<table>
<thead>
<tr>
<th>$T$, $^\circ$C</th>
<th>-20</th>
<th>-10</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>14</th>
<th>15</th>
<th>24</th>
<th>25</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric Constant, $\varepsilon$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dipole moment, $\mu$, Debye</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RI, $n_D$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4030</td>
<td>-</td>
<td>-</td>
<td>1.3970</td>
<td>-</td>
<td>1.3910</td>
</tr>
<tr>
<td>Specific Conductance, $K \times 10^2$</td>
<td>3.40</td>
<td>3.67</td>
<td>3.77</td>
<td>-</td>
<td>3.65</td>
<td>-</td>
<td>3.68</td>
<td>-</td>
<td>3.72</td>
<td>-</td>
</tr>
</tbody>
</table>
react explosively with concd nitric acid. In addition, furfuryl alcohol, aniline, etc are used with nitric acid in rocket fuels. Most metals, with the exception of the Pt metals and Au, are attacked by nitric acid, some are converted into oxides (As, Sb & Sn), but most are converted to nitrates. Metals which are not attacked are Al and Cr steel; these become passivated by the acid. Concentrated nitric acid will rapidly oxidize to a higher oxidation level the oxides, sulfides, etc of the lower oxidation states of most elements (Ref 34)

Again, according to Kirk & Othmer (Ref 34), the activity of nitric acid as an oxidizing agent is apparently dependent upon the presence of free oxides of nitrogen. Pure nitric acid does not attack Cu, for example, but when oxides of nitrogen are introduced, the reaction is at first slow and then proceeds with great rapidity and violence. The reduction products of nitric acid vary with the conc of the acid and the strength of the reducing agent with which it reacts. A mixt of oxides is generally produced; dil nitric acid tends to give a predominance of nitric oxide while concd acid produces a mixt richer in nitrogen dioxide. Very dil acid reacting with a strong reducing agent such as metallic Zn produces a mixt of ammonia and hydroxylamine.

Nitric acid also undergoes reactions with organic compounds wherein the acid serves neither as an oxidizing agent nor as a source of hydrogen ions. The formation of organic nitrates by esterification (O-nitration) involves reaction with the hydroxyl group:

$$ROH + HONO_2 \rightarrow RONO_2 + H_2O$$

Esterification with nitric acid includes the industrially important reactions with glycerol to form glyceryl trinitrate (trinitroglycerin), and with cellulose to form cellulose nitrate (nitrocellulose).

C-Nitration does not involve the hydroxyl group but is a reaction with an aliphatic or aromatic hydrocarbon or a substituted derivative to produce such compounds as the nitroaraffins and the nitrotoluenes:

$$R - H + HONO_2 \rightarrow RNO_2 + H_2O$$

These reactions are conceived to be with the positive "nitronium" ion $NO_2^+$, which is formed in nitric acid when free of w. These reactions therefore normally take place with a mixt of concd nitric and sulfuric acid, the sulfuric acid serving to remove the water formed.

In both the liq & the vapor phase, nitric acid decomp as $2HNO_3 \rightarrow 2NO_2 + H_2O + \frac{1}{2}O_2$ with a second equil with $NO_2 + 2NO_2 \rightarrow 2NO_2$. The rate determining step is the dehydration of $HNO_3$:

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

for the low-press vapor phase decomp within the 260–475° temp range (Ref 30)

Other techniques for decomping nitric acid are photochemical & flash photolysis. The photochemical decomp of nitric acid is not solely a gas-phase reaction; X-rays have caused the evolution of O₂ from nitric acid crystals. The use of flash photolysis has shown the nitrate radical to be an intermediate in the decomp (Ref 30)

See also under Nitration in this Vol Nitric Acid Explosives. According to Stetthammer (Ref 20), solns of aromatic nitrocompds in furning nitric acid are very powerful expls, which are inexpensive and simple to prepare. Such solns can be kept for several months in Fe or Al containers, even in sunlight, without decomp. These mixts can be transported in closed containers without danger of press rise.

When placed in air-tight Fe or Al containers, they can be used for underwater work. In such cases it is not necessary to insert the blasting cap into the acid charge, but merely to press it against the outside of the sheet metal with an insulating band. Since fuzes burn underwater, it can be lighted in the air, and the entire assembly then placed at the required depth.

When, for example, a mixt of NB is mixed in proper proportion with nitric acid, the resulting expl is as powerful as the corresponding amt of PA. This type of expl is known as a Sprengel type, ie, in which strong nitric acid is mixed with some combustible material or an expl. The expls Hiethofite and Dithekite consist of nitric acid and NB, and Oxonite contains nitric acid and PA.

An interesting plastic expl contg nitric acid was patented in 1887 by M. Jeschek & J. Jaesch of Vienna. It was prepd by adding 20 to 40% cellulose (cotton, straw, hemp, flax, etc) to a liq consisting of an aromatic nitrocompd and an amt of nitric acid sufficient to nitrate all the cellulose to NC, and to give a favorable OB to the mixt (Ref 4)

Also see under Liquid Explosives in Vol 7, L26-R
Other Uses of Nitric Acid. As mentioned earlier, fuming nitric acid (FNA) when mixed with alc., toluene or acet anhydrl will cause an expln. However, there are many other uses for FNA in energetic materials technology. As either red fuming nitric acid (RFNA) or as nitrogen tetroxide, it is used extensively as the oxidizer in propellent systems for ram-jets, jet motors, space rockets and other missiles (Refs 37, 38 & 39). See also under Liquid Propellants in Vol 7, L24-Rf

Another extremely important application area for FNA and RFNA is to either directly nitrate or be used in mixed acids to nitrate raw materials to yield widely used expls and propel/nt ingredients (Refs 29, 31, 33, 38 & 39). Also see under Nitration in this Vol Analytical. Analysis and assay procedures for nitric acid may be found in Refs 1, 2, 10, 11, 15, 17, 27, 29, 34, 35, and in this Vol under Nitrogen Determinations in Energetic Materials. For mgf plant electronic control systems see Ref 36; for plant chemical control procedures see Refs 3, 5, 14 & 26. USA Mil Specs are listed in Refs 29 & 35

Written by H. L. HERMAN


Addn Refs Not Used in Above Text:
1) F. Kuhlmann, Ann 29, 281 (1839) (Laboratory preparation of nitric acid by oxidation of ammonia in presence of catalysts) 2) H.R. Hoesner, IEC 9, 424 (1917) (Literature of
NITRIDES

Antimony Nitride. SbN, mw 135.76, N 10.32%, org cryst, mp 550–750°C (decomp exphy), bp 750°C (subl, decomp). Prepd by heating Sb to a dull redness in a current of N₂. Decomp explosively when heated or upon addition of cold w.

Bismuth Nitride. BiN, mw 223.01, N 6.28%, blk cryst, d 7.85/cc. Prepd from Bi tribromide or trioxide by reaction with potassium in liq ammonia. The dry nitride explos when treated with w or dil acids; sl decompn with w vapor.

Expnds when shaken, yielding Bi

Cadmium Nitride. Cd₃N₂, mw 365.22, N 7.67%, or cryst (tums blk), bp subl over 100°C, d 7.679/cc. Prepd by heating the amide, Cd(NH₃)₂ under vac for 3 hrs at 180°C. Compd is decompd by w and oxidized by air. Reacts explosively with dil acids and bases, and upon strong heating.

Cerium Nitride. CeN, mw 154.13, N 9.09%, bronze-blk cryst, mp 320–762°C (decomp). Prepd by heating Ce to 850°C and reacting with N₂. Reaction is sudden and violent, accompanied by a brilliant incandescence. It reacts violently with w, dil acids and moist air.

Chlorine Nitride. (Nitrogen Trichloride, Trichloramine, or Stickstofftrichlorid in Ger). NCl₃, mw 120.38, N 11.64%; yell, vol, pungent-smelling oil, mp < -40°C (Porret in 1813 reported -27°C), bp about 11°C (explds at 93–95°C), d 1.653g/cc. Soln in cold w (decompd by hot w), alc, eth, chlf, bz, CCl₄, CS₂ & phosphorous oxychloride. Prepd (with great care) by the action of sodium hypochlorite on amm chloride. The compd also forms at the anode in the electrolysis of concd amm chloride soln. Another prepn consists of bubbling chlorine into a cooled aq soln of amm sulfate & di-n-butyl ether (Reps 1, 6 & 10).

Bromine Nitride (Nitrogen bromide or Nitrogen tribromide). NBr₃ (probably), mw 253.74, N 5.52%, dark red volatile oil, strong smelling, which attacks the eyes. Prepd by action of NCl₃ on KBr (Reps 1 to 4). Bromine Nitride is very unstable and a powerful expl. It expls violently when brought into contact with P or As.

NITRIC ETHER. See under Ethane Nitrate in Vol 6, E143-R

NITRIC OXIDES. See under Nitrogen Oxides in this Vol
Exploids at 60° after 13 sec in a sealed glass tube (Ref 4). Exploids spontaneously when frozen and then thawed. Compd is a violent expl, extremely sensitive to impact or friction. It also exploids on exposure to strong light (sunlight or diffused), or when in contact with P, As, ozone, fused alkalies, and organic matter such as turpentine & rubber, but not with sugar or resins. Metals & strong acids do not cause it to explod. Qₚ 55 kcal/mole (Ref 9)

It is very poisonous & attacks the eyes & mucous membranes

Use. Too sensitive to use as an expl. The bz soln has been used for chlorinating org subjs

Analytical. Evolves N₂ quant when reacted with amm chloride


Copper Nitride (Cuprous Nitride). Cu₃N, mw 204.63, N 6.85%, v dk grn powd, mp 300° (decompn), d 5.84g/cc at 25/4°. Sol in conc HCl. Prepd by reaction of ammonia with Cu fluoride at 280°, and is stable at RT

The compd burns explosively at 470° and produces a flaming expln when heated quickly to 500° in air. It is not decompd by percussion or friction. Cu₃N is violently decompd on reaction with w, al, concd nitric & sulfuric acids. Decompd with dil mineral acids, no reaction with dil al or concd alkalies. Qₚ=17.8 kcal/mole; sp ht 0.1059 kcal/g/C


Fluorine Nitride (Nitrogen Fluoride or Nitrogen Trifluoride). NF₃, mw 71.01, N 19.73%, colorless gas having a moldy odor or mobile liq, mp −208.5°, fp > −216.6°, bp −128.8°, d (liq) 1.537g/cc at 129° & (gas) 0.1864lbs/cu ft at 70°F. V sl sol in w. Prepd by electrolysis of fused amm acid fluoride (Refs 2, 3, 4 & 5)

NF₃ exploids when mixed with hydrogen and kindled according to the equation: 2NF₃ + 3H₂ → N₂ + 6HF. It is a severe expln hazard, extremely sensitive to shock & blast. Reacts violently with reducing agents, grease & oil, etc. Highly toxic & corrosive to tissue. Qₚ > 29.7 ≈ 1.8 kcal/mole (Ref 6)

Use. Oxidizer for high energy fuels and in chemical synthesis (Ref 9)

Analytical. NF₃ can be quant analy by reaction with hot hydrochloric acid; NF₃ + 7HCl → NH₄Cl + 3HF + 3L₂; the iodine being titratd, or by reaction with sodium; 2NF₃ + 6Na → N₂ + 6NaF; the nitrogen being measured (Ref 3)


Iodine Nitrides. There are two compds of interest, the triiodide & the triiodide monamine, both of which are very sensitive expls

Nitrogen Triiodide. Nl₃, mw 394.77, N 3.55%, blk powd, mp (explds), hp (sbl in vac). Insol in cold w, decompd in hot w; sol in aq Na₂S₂O₃ and KCNS. Prepd by the action of gaseous NH₃ on solid KI₂, followed by rapid w washing (Refs 1, 4 & 10 & 11). Nl₃ must be kept ether wet. When dry, the slightest shock, vibration, temp rise, air draft, etc, will cause it to detonate (Refs 14 & 15). Under vac, dry Nl₃ detonates at pressures under 2x10⁻⁵cm. Over this press simple decompn occurs with the evolution of I₂ (Refs 7–9)
Nitrogen Triiodide Monoamine. (Nitrogen Iodoazoinide). \( \text{I}_2\text{N}:\text{NH}_3 \), mw 411.75, N 6.81%, dark red rhombic cryst, mp > 20° (decomp or expls), bp (explds), d 3.5g/cc. Sol in HCl, aq \( \text{Na}_2\text{S}_2\text{O}_3 \) and KCNS, decompd by w to \( \text{NI}_3 \). Prepd by adding an iodine chloride soln in HCl to an amonia soln (Ref 10).

I\( _2\)N:NH\( _3 \) detonates according to the equation: 8I\( _2\)N:NH\( _3 \) → 5N\( _2 \)+ 9I\( _2 \)+ 6NH\( _4 \). When dry, the compd can expld without apparent external cause (Refs 10–15). It will expld in contact with concd acids, bromine, chlorine, ozone and hydrogen sulfide (Ref 16). The initiation or activation energy is 19.0+1.3kg-cal. Q\( _F \) 35.0 kg-cal (Refs 8 & 9).

**Analytical.** I\( _2\)N:NH\( _3 \) can be quant analyzed by reaction with Zn ethyl: I\( _2\)N:NH\( _3 \)+3Zn(C\( _2\)H\( _5 \))\( _2 \) → 3ZnI\( _2 \)H\( _2 \)+NH\( _3 \)+N(C\( _2\)H\( _5 \))\( _3 \) & 2NH\( _3 \)+Zn(C\( _2\)H\( _5 \))\( _2 \)→Zn(NH\( _2 \))\( _2 \)+2C\( _2\)H\( _5 \). The liberated ethane is measured.


Mercury Nitride. Hg\( _3\)N\( _2 \), mw 629.78, N 4.45%, brown powd, mp (explds). Sol in amm hydride, dil acids, concd nitric acid and amm salts. Prepd by adding a soln of mercuric iodide or bromide to an excess of a soln of K amide in liq ammonia (Refs 1–3).

The compd is v exp & requires great care in handling. It will expld on heating, when struck with a hammer, or when rubbed. It explds when brought in contact with sulfuric acid.

Hg\( _3\)N\( _2 \) can be used as a dehydrogenating agent, viz, in liq ammonia soln it reacts with hydrazobenzene yielding azobenzene.


Potassium Nitride. K\( _3\)N, mw 131.31, N 10.67%, grn-blk cryst, mp 345°, ignites spontaneously in air. Effervescs violently w quantitatively evolving ammonia. Prepd by heating K amide to redness in a closed vessel or by striking an arc between a Pt cathode and a K anode under liq nitrogen (Refs 1–3).

K\( _3\)N puffs into flaming decomp when heated to 355°. It also unites with P or S when heated, forming a highly inflammable mixt.


Selenium Nitride (Nitrogen Selenide). Se\( _4\)N\( _4 \), mw 371.87, N 15.07%, yel-brick red hygr amorph powd, mp (expl 160–200°), bp (decomp). Si soln in hot w (decomp); v sl sol in acet, acet ac, bz & CS\( _2 \). Methods of prepn include passing dry ammonia into a dil soln of seleneyl chloride in bz, or into a cooled soln of selenium chloride in CS\( _2 \) (Refs 1–5 & 7–10).

Se\( _4\)N\( _4 \) expls violently on heating or when brought into contact with a drop of concd sulfuric acid. It is very sensitive to friction and impact. Q\( _F \)-169.2kcal/mole.

Silver Nitride. (Fulminating Silver). Ag₃N, mw 337.65, N 4.15%, blk-grey powd, mp 25° (start of decomp), d 9.0 = 1g/cc at 19°. Sol in weak acids, sl sol in q ammonia & sol in q solns of Na chloride and K cyanide. Prep by treating q Ag oxide with q ammonia soln, or by heating concd ammoniacal Ag chloride with solid KOH until evolution of ammonia ceases. The thoroughly washed product must be stored under w and, even so, is sensitive to touch (Refs 1–7)

Ag₃N explodes readily but is not very brisant. It explodes when illuminated with an electronic flash after receiving 0.2watts/sq cm of energy, and is unusually sensitive to mechanical action of any kind. Spontaneous expln occurs on heating from 100 to 165°. Contact with conc sulfuric acid will cause expl. Q₁ = 61.0kcal/mole (Refs 1, 2 & 5–9)


Sodium Nitride. Na₃N, mw 82.98, N 16.88%, drk grey powd, mp 300° (at 275° decomp), d 1.7g/cc at RT. Sol in w with quantitative evolution of ammonia. Prep by passing an electric arc between a Pt cathode and a Na anode under liq nitrogen (Refs 1–4)

Na₃N decomp appreciably at 150°, at 200° in about one hour, and at 350° in a few minutes. When heated rapidly nitrogen is evolved with expl violence (Refs 1, 2, 5 & 6)


Sulfur Nitride (Nitrogen Sulfide, Nitrogen Tetrasulfide). N₄S₄, mw 184.27, N 30.41%, golden-yellow to orange-red monclinic cryst, mp 175° (subl beginning at 135°), bp 185° (decomp), d 2.22g/cc at 25°, RI 2.046 at 4/20°. V sl sol in bz or CS₂; sl sol in alc, ether, tur-
NITRILES

Nitriles are organic derivatives of hydrocyanic acid in which the substituting group is attached to carbon. Their formula is R.CN. Because most nitriles can be derived from corresponding acid amides, R.CO.NH₂, by removal of w, they are called nitriles. For instance, the compd CH₂.CN is called acetonitrile because it is derived from acetamide. It can also be called methyl cyanide. The compd C₂H₃.CN is called either propionitrile or ethyl cyanide, etc.

The first nitrile to be prepared was propionitrile which J. Pelouze obtained in 1834 by distg Ba ethyl sulfate with K cyanide.

Some nitriles are expl, especially if they contain several −CN groups or a combination of −CN and −NO₂ groups. Other nitriles have been considered for use in double-base proplnts as they cool the flame and provide longer burning times; a variety of alkyl nitriles have been investigated as plasticizers (Ref 7).


LIST OF NITRILES

Acetonitrile and Derivatives. See Vol 1, A45-L to A46-R

Acrylonitrile and Derivatives. See Vol 1, A97-R to A98-L

Benzonitrile and Derivatives. See Vol 2, B76-R to B77-L

Cyanamide and Derivatives. See Vol 3, C580-L to C582-L
Cyanocompounds. See Vol 3, C583-L to C591-L

Diazaoacetonitrile. \((\text{N}_2)\text{CHCN}\), mw 67.06, N 62.68%, OB to CO\(_2\) -107.37%, orange-yl liq, fr p -18\(^\circ\), bp 46.5\(^\circ\) at 14-15mm Hg. Soln in w and eth. Prepd from the reaction of an aq soln of Na nitrite and aminoacetonitrile hydrochloride. The compd burns with a luminous flame. Expls violently on contact with Cu oxide and is friction sensitive. Its Hg salt is also an expl. 


1,2 Dicyanoethylene (Butandinitril in Ger, Succinonitrile, Ethylenecyanide or Ethylene-dicyanide). \(\text{NCCH}_2\text{CH}_2\text{CN}\), mw 80.09, N 34.98%, OB to CO\(_2\) -199.8%, colorl waxy subst. which can either be cryt or amorph, mp 53.7-54.5\(^\circ\), d 0.9899g/cc at 58.7\(^\circ\), 0.9980g/cc at 70/4\(^\circ\), 0.9649g/cc at 90/4\(^\circ\) and 0.950g/cc at 107.8/4\(^\circ\), R1 1.4165 at 63\(^\circ\). V soln in w, alc & chl; sl soln in eth. Prepd by adding dropwise a satd aq soln of KCN to a boiling soln of ethylene bromide in ethanol (Ref 2)

Dicyanoethane is an expl which is less powerful and less brisant than PA. Q 546.1kcal/mole. Viscosity 0.0276g/cm-sec at 58.7\(^\circ\) and 0.0181 at 83\(^\circ\) (Ref 4). The compd is very poisonous. 


Dicyanomethane (Methylenedicyanide, Malonocitrile or Propanedinitril). \(\text{NCCH}_2\text{CN}\), mw 66.07, N 42.41%, OB to CO\(_2\) -169.52%, colorl cryt, mp 31\(^\circ\), bp 223-224\(^\circ\), d 1.0506g/cc at 32.7/4\(^\circ\), 1.0338g/cc at 50/4\(^\circ\) and 0.9794g/cc at 107/4\(^\circ\), R1 1.4146 at 34.2\(^\circ\). Soln, w 13.45/100p, alc 40, eth 20, chl 10, ac acid 10, bx 6.7 (Ref 1). Prepd by heating cyanocacamide with PCl\(_5\) under vac at 100\(^\circ\) & then distg the product (Ref 2)

Dicyanomethane is an expl subst. less powerful and less brisant than PA. Q 395.1 kcal/mole, Viscosity is 0.0285g/cm-sec at 32.7\(^\circ\) and 0.0215g/cm-sec at 50\(^\circ\). The compd is very poisonous. 


Nitrilo Triacetic Azide (Triglykolamidsäure-triazid in Ger). \(\text{Ni(C}_2\text{H}_5\text{O})_3\text{N}_2\), mw 266.22, N 52.63%, OB to CO\(_2\) -72.12%, mp not found, leaflets. Soln in eth. Prepd from an aq soln of Na nitrite and nitrilotriacetic azide in eth. Very expl compd. 


Analytical Tests for Nitriles (Ref 6). 1) Redn. to the corresponding amines with Na & alc & identifying the amines by the usual methods; 2) Hydrolysis with aq KOH to ammonia, distn of the liberated NH\(_3\) into w & titratn of the resulting NH\(_4\)OH with H\(_2\)SO\(_4\) (Ref 3); 3) Hydrolysis to amides with KOH in diethyleneglycol or glycerin solns (Reps 4 & 5); 4) Treatment of nitriles with Grignard reagent to get ketones which form characteristic derivatives (Ref 1); and 5) Condensation with phloroglucinol by the Houben-Hoesch synthesis to give readily characterized phlorophenones (Ref 2) 


ISONITRILES. This designation includes isocyanides (see Vol 3, C582-L to C583-L and Vol 7, 1135-R for Cyanoic Acid and Derivatives) and Carbylamines, R.NC. The first isonitrides were prepd in 1886 by Gautier, by the action of Ag cyanide on alkyl iodides. Later, Hofmann prepd them by the action of chl & alc KOH on primary amines:

\[ \text{R.NH}_2 + \text{CHCl}_3 = \text{R.NC} + 3\text{HCl} \]

These compds are also formed during the prepn of nitriles, by heating aryl or aroylalkyl halides, or alkyl sulfure or phosphoric esters, or arylsulfonic esters with K or Na cyanide in alc.

The isonitrides are reactive, volatile liqs with an extremely repulsive odor. Their formation is often used as a method for the detection of primary amines. 

Reps: 1) Thorpe 8 (1947), 487 2) D. -
NITRILE OXIDES. Nitrile oxides are a well known class of comds represented by R.C:N=O, and are usually prepd by treating hydroxamic acid chlorides with a mild alkali, thus eliminating HCl (Ref 2). Wieland (Refs 1 & 3) was responsible for the first isolation of free nitrile oxides. These comds are somewhat unstable, showing a marked tendency to dimerize to the corresponding furoxanes (1,3-dipolar addition) (Refs 2 & 3). The nitrile oxides add to a considerable number of carbenes, as benzonitrile oxide (for example) to a large number of olefins in ether at 20° (Ref 3).

As shown below, several of the nitrile oxides are expls.

Refs: 1) H. Wieland, Ber 42, 803-816 (1909)

Triacetonitrile Oxide.

\[
\begin{align*}
\text{N} & \quad \text{C} \quad \text{C} \\
\text{O} & \quad \text{C}(\text{CH}_3) \\
\text{O} & \quad \text{C}(\text{CH}_3)
\end{align*}
\]

mw 167.14, N 25.15%, OB to CO\textsubscript{2} -110.04%; vitreous, brittle mass; mp 95° (decompn). Dissociated by boiling acids & toluene. Prep by reacting ethyl nitrolic acid & Na carbonate Triaconitrile oxide expls when heated on a spatula.

Refs: 1) Beil, not found 2) H. Wieland, Ber 42, 816-20 & CA 3, 1271 (1909)

Trichloroacetonitrile Oxide (2,4,6-Triphenyl-1,3,5-Triazine-Trioxide or Trimer Benzonitriloxide).

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C}(\text{C}_6\text{H}_5)
\end{align*}
\]

mw 357.39, N 11.76%, OB to CO\textsubscript{2} -208.18%, colorl cryst, mp 125-30° (decompn). Dissociated by alc, HCl, boiling toluene, acet ac, me alc, PCl\textsubscript{5} & bz chloride. Prep from phenylnitric acid and Na carbonate in 50% yield. It expls very readily when heated or in contact with coned sulfuric acid.

Refs: 1) Beil 26, 97 2) H. Wieland, Ber 42, 803-16 & CA 3, 1270-1 (1909)

Trifuralin (1,3,5-Triazine-Trioxide, Trimery Formonitriloxide or Tris-Formonitriloxide).

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{O} & \quad \text{C} \\
\text{N} & \quad \text{C}
\end{align*}
\]

mw 129.09, N 32.56%, OB to CO\textsubscript{2} -92.96%, colorl powd, mp not available. Dissoc by w into formhydroxamic acid. Prep from anaq soln of methylnitrolic acid when reacted with ammonia or Na carbonate. Yield is 85%. It expls in contact with either coned sulfuric or coned hydrochloric acids.

Refs: 1) Beil 26, 34 2) H. Wieland, Ber 42, 803-16 & CA 3, 1270-1 (1909)

NITRIMINES

Compds of the general formula R\textsubscript{2}C=N-NO\textsubscript{2}.
The first compd of this kind was prepd in 1895 by Angeli et al upon treating camphoroxime with nitrous acid. Similar compds were obtained from a number of terpenoid ketones. Angeli called the resulting substances “perimtroso” derivatives and assigned to them structures of either R\textsubscript{2}C=N-O-NO or R\textsubscript{2}C=(NO)\textsubscript{2} (Refs 1 & 2)

Scholl et al (Refs 3 & 4) prepared the same compds by treating ketoximes (such as pinacolone) with nitrogen tetroxide, but he assigned them the structure R\textsubscript{2}C=N-NO\textsubscript{2} and called them nitrimines. One of the compds described by him in Ref 4, p 27 is a weak exp. It is the Ag salt of pinacolone-nitraminic acid which puffs off on rapid heating (this compd described below under “List of Nitrimines”). Further work on
Nitrimes was done by Harries et al (Reps 5 & 6), Fusco et al (Ref 10), Hantzh (Ref 7), Ponzo (Ref 8), and Saccardi and Latini (Ref 9). Suggitt et al gave a brief general review on nitrimes and described the prepn and properties of many of these compds (Ref 11).

Nitrimes seem to exist in several isomeric forms and their structures have not been definitely established. For instance, four different structures for mesityl nitrime are given by Suggitt et al in Ref 11.

A discussion of nitrimes usage as energetic materials is part of the article entitled "Amines Nitrated and Nitrited" in Vol 1, Al74-R to A178-R.


LIST OF NITRIMINES

Dicyandiamidine & Derivatives. See Vol 5, D1217-L to D1218-L.

Hexanitrodiphenylguanidine. Note: guanidines are included here, although A.F. McKay et al (Ref 4) states "... these compds should not be classed as guanidines".

\[(\text{NO}_2)_3 \text{C}_6 \text{H}_3 \cdot \text{N}.\text{C}.\text{N}.\text{C}_6 \text{H}_5 (\text{NO}_2)_3, \text{C}_2 \text{H}_7, \text{N}_2 \text{O}_2, \text{NH}
\]

\[\text{mw 481.29, N 26.20%, OB to CO}_2 \text{ -58.18%}
\]

Prepn not found. Hexanitrodiphenylguanidine is an expl claimed to be less sensitive and 1/3 more powerful than Tetryl (Ref 2).


Nitroquanidine and Derivatives. See Vol 6, G154-Rff.

3-Nitro-5-Imino-1-Benzoyl-Cyclopentene-1.

\[\text{H}_2 \text{C} \cdot \text{C} \cdot (\text{NH}) \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6 \text{H}_5\]

\[\text{O}_2 \text{N} \cdot \text{H} \cdot \text{C} \cdot \text{C}_6 \text{H}_5 \text{CH}
\]

\[\text{C}_12 \text{H}_10 \text{N}_2 \text{O}_3, \text{mw 230.24, N 12.17%, OB to CO}_2 \text{ -180.68%, brn-yel amorph mass, mp 127-132\(^\circ\) (decomp). V sol in chlf, acet, et acet, glc acet ac; sl sol in alc and benz; insol in eth, lig and w. Prepd by the reaction between 4-nitro-2-phencyl-4-pyr with the hydrochloride of \(\beta\)-amino-propioiophenon in aq alc soln of NaOH at 50\(^\circ\).

Ref: 1) Bell 7, (386); Note: Bell does not differentiate between a nitrime and a nitroline. Both compd types are listed under "Nitroimines" by Beil and are so presented here. Perhaps this method of presentation is because of the lack of a nitrime structural definition.

Alpha'-Nitro-Alpha'-Imino-Dibenzy1-Carbonic acid-2. C_{15}H_{14}N_2O_4, C_6H_5.CH(NO_2).C(NH).C_6H_4.CO_2H, mw 284.29, N 9.86%, OB to CO_2 -180.10%, sulfur-yel cryt, mp 147-150\(^\circ\) (decomp). Prepd by warming alpha-nitrobenzal-phthahalinidin with dil aq NaOH.

Ref: 1) Bell 10, 757.

[N-Nitro-Imidodiacetic Acid]-bis-[2,4-Dinitro Anilide]. C_{16}H_{12}N_4O_2, [(O_2N)_2C_6H_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2]_2 \text{N}.\text{NO}_2, \text{mw 508.36, N 22.04%, OB to CO}_2 -119.60%, sulfur-yel leaflets, mp 214-15\(^\circ\) (decomp). Soln in nitrobenz and dil KOH. Prepd by reacting imidodiacetic acid-dianilide with anhydr nitric acid at the fr p of the reactants.

Ref: 1) Bell 12, (364).

Nitroiminodiacetic Acid (Nitrogiylanidic Acid). C_{5}H_{6}N_{2}O_{5}, C_{2}N_{2}N(\text{CH}_2).\text{CO}_2\text{H}_2, \text{mw 278.12, N 15.73%, OB to CO}_2 -44.91\%, cryt, mp 148-155\(^\circ\) (decomp). Soln in w, methanol, et alc, acet and et acet; insol in chlf and benz. Prepd by briefly heating imidodiacetic acid with anhydr nitric acid.

Nitroiminodiacetic acid forms expl metallic salts; viz, Copper Nitroiminodiacetic Acid, Cu_{6}C_{4}H_{6}N_{2}O_{6}, is a greenish microcryst powd which explds on heating.
Dipotassium Nitroiminodiacetic Acid, K$_2$C$_4$H$_4$N$_2$O$_6$, cryst plates whose expln temp is 195°.

Silver Nitroiminodiacetic Acid, Ag$_2$C$_4$H$_4$N$_2$O$_6$, a wh ppt which expls on heating.

Zinc Nitroiminodiacetic Acid, ZnC$_4$H$_4$N$_2$O$_6$, cryst which expls on heating

Ref: 1) Beil 4, (488)

Nitroiminodiacetic Acid Diamide (Nitrodiglycolamidic Acid). C$_6$H$_5$N$_2$O$_4$, O$_2$N.N(CH$_3$.CO.NH$_2$)$_2$, mw 176.16, N 31.81%, OB to CO$_2$ 72.66%, clear platelets, mp 190–218° (decompn). Prepd by nitratn of iminodiacetic acid amide with anhydrous nitric acid at RT

Ref: 1) Beil 4, (488)

Nitroiminodiacetic Acid Dinitrile (Nitrodiglycolamidic Acid Dinitrile). C$_6$H$_4$N$_2$O$_2$, O$_2$N.N(CH$_3$.CN)$_2$, mw 140.12, N 39.99%, OB to CO$_2$ 91.35%, colori ndls, mp 98° (softens); 104–5° (decompn). Sparingly sol in benz, eth, alc and et acet; sol in w and chlf; insol in petr eth. Prepd by nitratn of iminodiacetic acid dinitrile with anhydronic acid at RT

Ref: 1) Beil 4, (488)

N-Nitro-[Alpha, Alpha'-Imino Diproponic Acid]. C$_6$H$_9$_N$_2$O$_4$, O$_2$N.N[CH(CH$_3$).CO.H$_2$], mw 206.18, N 13.59%, OB to CO$_2$ 85.36%, cryst, mp 175–80° (decompn). V sol in alc, methanol, acet; sol in et acet, chlf, benz and cold w; also sol in cold concd HCl. Prepd by warming alpha, alpha'-imino-diproponic acid with anhydronic acid

Ref: 1) Beil 4, (498)

N-Nitro-A, Alpha'-Imino Diproponic Acid. (1-Nitro-3,5-Dioxo-2,6-Dimethyl Piperazine).

HN \[ \text{CO.CH(CH$_3$)} \] \[ \text{N.NO$_2$} \], C$_6$H$_9$N$_2$O$_4$, mw 187.18, N 22.45%, OB to CO$_2$ 106.85%, ndls, mp 136–38° (decompn). Sparingly sol in cold w. Prepd by nitratn of alpha, alpha'-iminodiproponic acid imide with anhydronic acid

Ref: 1) Beil 24, (309)

Pinacoline Nitraminic Acid. C$_5$H$_4$.N$_2$O$_2$, (CH$_3$)$_3$.C.N.N.O$_2$, mw 131.18, N 21.36%, OB to

CO$_2$ 164.66%, oil, bp 80–85°/11mm. Sol in eth. Prepd by reacting pinacoline oxime in dry eth with fresh liq N$_2$O$_4$ at -10° (Ref 3)

The Ag salt of pinacoline nitraminic acid, or Silver Pinacoline Nitraminic Acid, AgC$_5$.H$_4$.N$_2$O$_2$, is a weak expl which puffs off on rapid heating (Ref 2)


**NITRITES**

Nitrates are the salts of nitrous acid, discovered by Scheele in 1774. The inorganic nitrates, with the general formula M.NO$_3$, where M is a metal, are well known. They are all insol in w with the exception of the alkali nitrates. Nitrates may be prepd either by thermal decompn of alkali nitrates; 2KNO$_3$ → 2KNO$_2$ + O$_2$, or by reduction of nitrates by C or Pb; 2KNO$_3$ + C → 2KNO$_2$ + CO$_2$. The lone pair of electrons in the nitrite ion is sterically significant; consequently, the nitrite ion is bent:

\[
\begin{align*}
\text{O} & \quad \leftrightarrow \quad \text{O} \\
\text{N} &
\end{align*}
\]

The N-O bond distance has been reported as 1.24 Å with a bond angle of 115° (Ref 3). The salts as well as the acids act both as oxidizing and reducing acids. The principle use of the inorganic nitrates is in organic synthesis, including diazotization. *When heated with thiosulfates or cyanides, nitrates detonate violently* (Ref 4)

The so-called nitrite comps, having the same formula as nitro comps, RNO$_2$, are not identical with them, and should be represented by the formula R.O.NO:

LIST OF NITRITES

Ammonium Nitrite. See Vol 1, A380
Addnl Ref: Ephraim (1954), 723

Amyl Nitrite. See Vol 1, A397-R

Barium Nitrite. Ba(NO₂)₂, mw 229.38, N 12.21%, mp 217°C, d 3.19g/cc at 23°C; and Ba(NO₂)₂·H₂O, mw 247.38, N 11.32%, mp decomps 115°C, d 3.17g/cc at 29°C. Both salts are colorless to yellow crystals, and are very soluble in water, slightly soluble in alcohol and insoluble in ether. Prepared by the methods described in Refs 1 & 2. Highly toxic by ingestion. Used in diazotization reactions, prevention of corrosion of steel bars, and in explosives.

Refs: 1) Gmelin, Syst Nr 30 (1932), 149-64 & Supplement (1960), 178-79, 305-16
2) Mellor 8 (1946), 485-88
3) Parfitt (1950), 551
4) Merck (1968), 121-R
5) CondChemDict (1971), 93-R
6) Hackh's (1972), 79-L

Copper Diammoniumnitrites. See under Ammoniates in Vol 1, A275ff

Ethyl Nitrite. See under Ethane Nitrite in Vol 6, E145-L

Hydrazine Nitrite. See in Vol 7, H196-R

Methyl Nitrite. See under Methyl Nitrite in this Vol

Potassium Nitrite. KNO₂, mw 85.10, N 16.46%, white or slightly yellow, deliquescent, melts at 182°C (decomps at 350°C), bp 1000°F, d 1.915g/cc. Soluble in 0.35g water, slightly soluble in alcohol. Prepared by the methods described in Refs 1 & 2. It is decomposed by weak acids with evolution of brown fumes of nitrous anhydride (Ref 1).

KNO₂ detonates violently when heated in the presence of thiocyanates or cyanides. Ref 1 states that when mixed with K cyanide, the mixture burns, and at 450°C, it explodes violently. Ref 6 details instances of molten KNO₂ being violently decomposed by boron, and of a vigorous reaction attended by flame caused by the addition of a little ammonium sulfate to fused KNO₂.

Its primary uses have been in analytical chemistry (testing for amino acids, Co, I₂ and urea), in medicine, and in organic synthesis.

Refs: 1) Mellor 8 (1946), 473-4 & 478
2) Parfitt (1950), 551
3) Merck (1968), 856-L
4) CondChemDict (1971), 723-R
5) Hackh's (1972), 540-R

Propyl Nitrite. See Propyl Nitrite under P

Sodium Nitrite. NaNO₂, mw 69.01, white or yellow hygroscopic crystals, melts or powders, mp 271°C, bp 1000°F, decomps at 320°C, d 2.157 g/cc. Oxidizes slowly to nitrate in air. Soluble in 1.5g cold water, 0.6g boiling water; slightly soluble in alcohol. Prepared by the methods described in Refs 1 & 2. Decomposed by weak acids with evolution of brown fumes of N₂O₅.

When mixed with Na thiosulfate or cyanide salts and heated, violent explosions occur. A similar reaction occurs if an ammonium salt is melted with a nitrite salt. NaNO₂ at 460°F in contact with the fiber drums in which it is shipped undergoes a vigorous decomposition reaction producing a propellant-type burning until the carton is consumed (Ref 6).

NaNO₂ is used for diazotizing in dyestuff manuf., in org synthesis, rubber accelerators, prep of nitric oxide, pharmaceuticals, photographic reagents, curing meats, dyeing and printing textile fabrics, etc.

Refs: 1) Mellor 8 (1946), 473-4 & 478
2) Parfitt (1950), 551
3) Merck (1968), 963-L
4) CondChemDict (1971), 806-L
5) Hackh's (1972), 620-L

Nitrito- Compounds. Organic compounds containing one or several -O.N:O groups which are called oxynitroso radicals. These compounds are also known as organic nitrites. Some are expls, as, for example, Methyl Nitrite, CH₃NO. (see in this Vol). They are not as stable as the corresponding nitrates and nitrocompounds.

Ref: Hackh's (1972), 457
Nitritodimercuriacetaldehyde.
OHC.C(Hg).Hg.O.NO, mw 488.26, N 2.87%, OB to CO₂ & HgO —11.5%, golden yel powd. Prepd by passing acetylene thru a soln of mercuric nitrate in 1% nitric acid in the presence of an excess of K nitrate. The dry compd explds on heating or by friction
Refs: 1) Bell 3, 606  2) K.A. Hofmann, Ber 38, 2004 (1905)

Nitroacetaldoxime. See Methazonic Acid in Vol 1, A16-L, listed as Mononitroacetaldoxime under Acetaldoxime

Nitroacetic Acid. See Vol 1, A27-R under Acetic Acid and Derivatives. Its dipotassium salt, which is exp is briefly described, whereas its other exp salts, such as Pb, Ag and Hg are only mentioned. All of these salts are described by W. Steinkopf in Ber 42, 2026-31 (1909) & CA 3, 1438 (1909)

Nitroacetin. Same as Glycerin Acetate Dinitrate. See Dinitroacetin in Vol 1, 33-L, and as Glycerol Dinitrate Monoacetate in Blatt, OSRD 2014 (1944)

Nitroacetonitrile. See under Acetonitrile and Derivatives in Vol 1, A45-R

Nitroacid. A compd containing both the radicals —COOH and —NO₂. Some of these are exp, eg, Nitroacetic Acid, O₂N.CH₂.COOH; Dinitrobenzoic acid, (O₂N)₂.C₆H₅.COOH; Trinitrobenzoic acid, (O₂N)_3.C₆H₅.COOH; etc
Ref: Hackh’s (1972), 457-R

Nitroagave. See under Agave in Vol 1, A110-L

Nitroalbuminoids. Albuminoid products usually include glue, bones, hair, feathers, etc. The nitration of these materials with mixed nitric-sulfuric acids, in two stages, for the prepn of exps, is detailed in the Ref
Ref: V. Gallarati, BritP 358116 (1930) & CA 26, 6141 (1931)

Nitroalkanols, R.CH(OH)CH₂.NO₂; Nitroalkanol Nitrates, R.CH(O.NO₂).CH₂.NO₂ and Dinitroalkanes, R.CH(NO₂).CH₂(NO₂). These compds, suitable for use in expl compns, may be prepd by treating olefins with 3 to 6 atoms with an ethereal soln of N₂O₄ in the presence or absence of O₂. For example, when propylene, CH₃CH=CH₂, is bubbled thru a soln of N₂O₄ in methylated ether in the presence of O₂, a mixt of (1) 1-Nitropropanol-2, CH₃.CH(OH).CH₂(NO₂); (2) 1-Nitropropanol-2-nitrate, CH₃.CH(O.NO₂).CH₂(NO₂) (bp 71°); and (3) 1,2-Dinitropropane, CH₃.CH(NO₂).CH₂(NO₂) (bp 88°), is obtained. For the best yields of compd (1), the O₂/olefin ratio should be less than 0.15/1; for high yields of (2), more than 0.25/1; and for (3), the reaction should be conducted in the absence of O₂

Nitroaminocompounds or Nitroamines. Compds containing both —NO₂ and —NH₂ radicals attached to different C atoms, eg, nitroaniline, O₃N.C₆H₄.NH₂, etc. Nitroamines can be prepd either by the nitration of amines, or by partial reduction of nitrocompounds contg several —NO₂ groups. Another method is to treat a chloronitrocompound with ammonia, as in the prepn of dinitroaniline

Nitroamines differ from Nitramines in that the latter contain either —NH.NO₂ or =N.NO₂ radicals, each attached to one C atom.

Some nitroamines are exp. The following are examples:
2,4-Dinitroaniline, (O₂N)₂.C₆H₄.NH₂. See in Vol 1, A408-R
2,4,6-Trinitroaniline, (O₂N)₃.C₆H₄.NH₂. See in Vol 1, A409-R
2,4,6-Trinitro-3-aminobisole, (O₂N)₂.C₆H(OCH₃).NH₂. See in Vol 1, A182-L

2,4,6-Trinitro-3-aminophenetole, (O₂N)₃.C₆H(OCH₃).NH₂. See in Vol 1, A240-R
4,6-Dinitro-2-aminophenol, (O₂N)₂.C₆H₂(OH).NH₂. See in Vol 1, A241-R
Refs: 1) Sidwick (1937), 73—4  2) Houben 4 (1941)  3) Hickinbottom (1948), 320—21
Nitroaminoguanidine. See in Vol 1, A210-Rff

Nitroamylene glycol (Nitro-iso-amylglycol, 2-Nitro-2-methylol-butanol-(1), Nitropentanediol). 
(O₂N).C(C₂H₅).CH₂OH₂ or 
CH₃.CH₂.C(NO₂).(CH₂.OH)₂. mw 149.15. N 9.39%, OB to CO₂ -123.4%, white needles from w, mp 58.8°, bp decomp. Prepd either by treating 1 mol of secondary nitro-normal butylic alc, (O₂N).CH(C₂H₅)(CH₂OH), with 1 mol of formaldehyde in the presence of a small amt of anhyd K carbonate, or by treating 1 mol of primary nitropropane with 2 mols of formaldehyde in the presence of K carbonate.

Nitroamylene glycol is v sol in w, sol in alc and eth. On nitration it yields an expl dinitrate (see below).

Refs: 1) Beil 1, 483 2) J. Pauwels, JCS (Abs) 74 (1), 506-7 (1898)

Nitroamylene glycol Dinitrate (Nitro-iso-amylglycol Dinitrate). (O₂N).C(C₂H₅).CH₂.O.NO₂)₂ or 
CH₃.CH₂.C(NO₂).(CH₂.O.NO₂)₂, mw 239.15. N 17.57%, OB to CO₂ -43.5%, yel viscous oil.
Prepd by Bergeim (Ref 2) by the nitration of nitroamylene glycol with mixed acid containing 40% nitric and 60% sulfuric

It is an expl with properties resembling those of Nitro-iso-butyl glycol Dinitrate, and was proposed for use in Dynamites as either a substitute for, or in conjunction with NG. It may also be used in double-base proplants.

Refs: 1) Beil — not listed 2) F.H. Bergeim, USP 1691955 (1928) & CA 23, 708 (1929)

Nitroanilines. See under Aniline in Vol 1, A406ff

Nitroanisoles. See under Anisole and Derivatives in Vol 1, A448ff

Nitroarabinose. See under Arabinose and Derivatives in Vol 1, A476

Nitroazido Compounds. See under corresponding Azido compound

Nitrobaronit. An early type of aluminized expl.
Two formulations which were tested by the Commission des Substances Explosif are shown below:

<table>
<thead>
<tr>
<th>Nitrobaronit</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amm Nitrate</td>
<td>82</td>
<td>69</td>
</tr>
<tr>
<td>Al</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>NG</td>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td>NC (12% N)</td>
<td>—</td>
<td>0.75</td>
</tr>
<tr>
<td>Liq DNT</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Wood flour</td>
<td>1.5</td>
<td>1.25</td>
</tr>
<tr>
<td>Petr pitch</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>C.U.P.</td>
<td>124% of PA</td>
<td>125.5% of PA</td>
</tr>
</tbody>
</table>

C.U.P. (Coefficient d'utilisation pratique) is the same as for Pb block expansion, as compared with PA (100%).
Ref: L. Méard, MAF 22, 596 (1948)

Nitrobellite. Same as Bellite, see Vol 2, B32-R

Nitrobenzaldehyde. See under Benzaldehyde and Derivatives in Vol 2, B35

Nitrobenzamide. See under Benzamide and Derivatives in Vol 2, B38-R

Nitrobenzene. See under Benzene and Derivatives in Vol 2, B41-Rff

m-Nitrobenzenediazonium Perchlorate (m-Nitrodiazobenzeneperchlorate). 
O₂N.C₆H₅.N(ClO₄)₄.N , mw 235.57, N 16.89%, OB to CO₂ -54.3%, mp explds at approx 154°, hygr crysrs. Prepd by dissolving m-nitroaniline in an excess of dil perchloric acid (d 1.12g/cc), the excess being such that, at the end of the reaction, free acid is present. A sufficient quantity of Na nitrite, in solid form or in a satd soln, is added to effect diazotization. The mixt is cooled during the Na nitrite addition:

O₂N.C₆H₅.NH₂+HClO₄+HNO₂→O₂N.C₆H₄N(ClO₄):N+2H₂O

For more details of the prepn, see Davis (Ref 4)

Nitrobenzenediazonium perchlorate is sl sol in w. It is an expl, sensitive to impact and
friction and of not very satisfactory thermal stability. It was patented in 1911 by von Herz (Ref 2), and has been used in Ger in compound detonators, using as a base charge, Nitromannite, or other brisant nitric esters. Other perchlorates of diazocompounds of aromatic hydrocarbons, such as those of toluene, naphthalene, anthracene, etc., were also recommended by von Herz. Refs: 1) Beil — not found 2) E. von Herz, GerP 258679 (1911) & CA 7, 2687 (1913) 3) Colver (1918), 738 4) Davis (1943), 442

Nitrobenzene Dynamite. A Belg blasting powd, manufd at the turn of the century. It contained NG 86, NC 10 and NB 4% Ref: Daniel (1902), 493

Nitrobenzoic Acid. See under Benzoic Acid and Derivatives in Vol 2, B69-Rf

Nitrobenzoic Dynamite (Dynamite Nitrobenzoique). An expl patented in 1882 in Fr contg NG 15 to 45, NC 1 to 3, NB 5 to 10 and AN 50 to 73 Ref: Daniel (1902), 783

Nitrobenzol. Same as Nitrobenzene

Nitrobenzoyl. The monovalent radical, O₂N.C₆H₄.C₂O−, derived from nitrotoluene by replacing a hydrogen of the methyl group

o-Nitrobenzoyl Chloride. O₂N.C₆H₄.C₂OCl₂, mw 185.57, N 7.55%, OB to CO₂ 112.1%, colorless crysts, mp 24–25°, bp 148–51° at 12mm. Sol in ether, decompd by w or alc. Explds in the presence of organic impurites.

May be prepd by heating 2-nitrobenzoic acid with 5p of thionyl chloride, SOCl₂, and then distg off the excess SOCl₂ by heating under vac on a w bath for 4–5 hours. Several explns (Refs 2 & 3) have been reported during the prepn, although the temp was at 100°. In order to avoid such explns, it has been proposed (Ref 3) to carry out all reactions in soln, using only very pure materials. For example, if pure 2-nitrobenzoic acid is dissolved in benz, treated with one mol of pure SO₂, and refluxed until the evolution of SO₂ and HCl has ceased, the procedure seems to be safe. Another method of prepn consists of heating dry 2-nitrobenzoic acid together with 50g of PCl₅ on a w bath for 1–1½ hours, and then distg the resulting POCI₃ under reduced press. Yields in both methods of prepn are about 85%

Note: o-Nitrophenylacetyl Chloride,

Nitrobenzyl. The monovalent radical, O₂N.C₆H₄.C₂H₄—, derived from nitrotoluene by replacing a hydrogen of the methyl group

Nitro-bis-Benzenediazonium Perchlorate (Nitro-bis-Diazobenzene Perchlorate).
O₂N.C₆H₄.[N(ClO₄)₂], mw 376.04, N 18.63%, OB to CO₂ 14.9%. This compd was prepd and patented by von Herz (Refs 2 & 3) for use in detonators. It has been claimed that this perchlorate is more stable and effective as an initiator than the azides Refs: 1) Beil — not found 2) E. von Herz, GerP 258679 (1911) 3) Marshall 2 (1917), 512

Nitrobran. See under Bran in Vol 2, B260-R

Nitrobutane. See under n-Butane and Derivatives in Vol 2, B366-Rf

Nitrobutanol Nitrate (Nitrobutylic Nitrate, 2-Nitro-butanol-(1)-nitrate).
O₂N.CH(C₂H₄).CH₂(ONO₂), mw 164.12, N 17.07%, OB to CO₂ 68.2%, yellowish, somewhat visc liq, d 1.242g/cc at 15.5°. Prepd by Pauwels (Ref 2) by nitrating secondary nitro-normal bu-
tylic acid, \( \text{O}_2 \text{N.CH(C}_2 \text{H}_5)\text{CH}_2 \text{OH} \), with mixed
nitric-sulfuric acid. It is a mild expl

Refs: 1) Beil 1, 370 2) J. Pauwels, Rec 17, 27–49 (1898) & JCS (Abs) 74 (1), 507

**Nitroisobutylglycerin** (2-Nitro-2-methylol-1,3-
propanediol, 2-Nitro-2-oxymethyl-1,3-propane-
diol). \( \text{O}_2 \text{N.C(CH}_2 \text{OH)}_3 \), mw 151.12, N 9.26%,
OB to \( \text{CO}_2 \) \( \text{79.4}, \) mp 144–180°. Note: Ac-
gording to Beil 1, [596] it exists in two mod-
fications, one melting (not sharply) at 144°, and
the other at 180°. The second form is obtained
by treating the first form with either sulfuryl-
chloride or phosphorus trichloride. After
cryst from ethyl acetate & chl, a substance is
obtained which melts sharply at 180°. On
standing, the second form slowly reverts to
the low melting modification. It is usually found
in the form of needles and crystals, and is sol in
w, alc and eth.

Nitroisobutylglycerin can be prep by several
methods, all of which have been tried at PicArsn
(Ref 9). The procedure described by Stettbacher
(Ref 7) seems to give the best results, and is
based on the reaction, \( \text{(O}_2 \text{N)CH}_3 + 3\text{HCHO} \rightarrow \text{(O}_2 \text{N)(CH}_2 \text{OH)}_3 \). Add to a 3-necked 1-liter
reaction flask (set in a casserole filled with
cold w, and placed on a cold hot plate) 150g
of nitromethane and 2g of K carbonate hemi-
hydrate. Gradually add about 200g of 37%
formaldehyde, maintaining the temp in the flask
below 30°. Add gradually, in about 30 minutes,
an addl 475g of 37% formaldehyde, allowing the
temp of the mixt to rise to 80°. Maintain
the soln at 90° for 2 hours, connect the flask
to a 4° vac and evap to about 1/2 its vol to
drive off the bulk of the formaldehyde. Break
the vac, dil with w and conc again under re-
duced press. Repeat dilutions and concs until
only a faint odor of formaldehyde remains.
After allowing the mixt to cool, separate the red-
colored ppt by filtr. Dissolve the crude product
in hot alc and crys by cooling. Recrystallize
several times from eth.

On nitratation it yields an expl trinitrate (see
below)

Refs: 1) Beil 1, 320, (276) & [596]
2) L. Henry, BullSocChim [3], 13, 1001 (1895)
3) F. Hofwimmer, SS 7, 43 (1912) & CA 6,
1228 (1913) 4) E. Schmidt & R. Wilkendorf,
Ber 52, 392 (1919) 5) Nao’sm, NG (1928),
239–40 6) I.M. Gorski & S.P. Makarov,
Ber 67, 996–1010 (1914) 7) A. Stettbacher,
NC 5, 159–62, 181–84 & 203–06 (1934)
8) G.A. Hnold, SS 30, 263 (1935) 9) H.
Aarsonson, PATR 1125 (1941), 5

**Nitroisobutylglycerol Trinitrate (NIBGTN).**
\( \text{O}_2 \text{N.C(CH}_2 \text{ONNO}_2)_3 \), mw 286.12, N 19.58%
(Nitrat N=14.69%), OB to \( \text{CO}_2 \) ±0; thick,
yellowish, odorless oil which is more viscous
than NG; mp, did not freeze at –50°; bp, de-
comps or deflagrates in 5sec at 180–85° with-
out deton, detonates when heated with flame in
a sealed capillary tube; d 1.64g/cc at 20°
(1.68g/cc according to Hofwimmer & Nao’sm);
RI 1.4896 at 25°, 1.4874 at 30°. Insol in w,
CS2 and petr eth; sol in methanol, ethanol,
acet, eth, benz & ethylendichloride

Preparation. Can be prep by nitration of nitro-
isobutylglycerol. Following is the method pro-
poused by Stettbacher (Ref 7) and repeated at
PicArsn (Ref 10): Add gradually with mechanical
stirring, 50g of nitroisobutylglycerol to 304g of
mixed acid with compn \( \text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O} \)
38/60/2. The addition should be made in about
1/2 hour while maintaining the temp at below
15°. Stir for an addnl 1/2 hour while cooling
the mixt to 5°. Transfer the mass to a separa-
tory funnel, allow to stand for a while, and
draw off the bottom layer of acid. Wash the re-
sidual oil with w, then with aq Na bicarbonate,
and finally with w to neutrality to litmus (2
washes). Collect all the washings, mix them with
the spent acid, cook the liq and extract with eth.
Wash the eth extract with w, evap the ether,
add the oil from the separatory funnel and dry
the product in a vac desiccator. The yield was
about 95% of theoretical. Nitrate nitrogen con-
tent, as determined by nitrometer, gave only
14.12% as against 14.69% theoretical, which
indicated that the product was impure

Note: Due to the high viscosity of NIBGTN, its
purification by the above described method is
usually accompanied by formation of emulsions,
which delay the separation of the oil from the
aq solns. Much better results are claimed by
Crater’s method (Ref 9), in which the crude
product is washed twice with equal vols of w at
43.5°, and then by concd aq solns of Na sulfate,
while agitating the mixt by bubbling compressed
Nitro-iso-butylglycol (2-Nitro-2-methylpropanedioi-1,3, Tertiary Nitrodihydroxybutane, Nitroisobutyleneglycol).  $H_2C.C(NO_2)(CH_2OH)_2$, mw 135.12, N 10.37%, monoclinic crystals, mp 139–40°. Sol in w, alc and acet; sl sol in eth. Can be prepd by treating an aq soln of nitroethane and formaldehyde with a little K carbonate or bicarbonate. On nitration it yields an exp1, Nitroisobutylylglycol dinitrate (see below)
References: 1) Beil 1, 480 & [547] 2) L. Henry, CR 121, 210 (1895); JCS (Abs) 70 (1), 4 (1896) 3) J. Böcksen, Rec 39, 181 (1920) & CA 14, 2472 (1920)

Nitro-iso-butylglycol Dinitrate (NIBGkDN, 2-Nitro-2-methylpropanedioi-1,3-Dinitrate).

$H_2C.C(NO_2)(CH_2ONO_2)_2$, mw 225.12, N 18.67%, OB to CO$_2$ −24.9%; yellowish, odorless oil. Insol in w; v sol in eth, alc, benz and chlor.
Can be prepd as recommended by Bergeim (Ref 2) by gradually adding nitroisobutylylglycol to a stirred mixed acid of approx 40% nitric and 60% sulfuric acid by wt, keeping the temp at 5 to 10°. After allowing the mixt to stand, the oil collects on the surface, from where it is separated and purified by means of w and Na sulphate.

NIBGkDN is an exp1 of great strength, resembling Nitroisobutylglycerol in its properties but being less viscous, and hence more easy to handle during its manuf. It can be used either as a substitute for NG, or in conjunction with it and the other usual ingredients of Dynamite to yield a powder of good strength and sensitivity. Following is a typical formulation of such a Dynamite: NIBGkDN 15, NG 15, Na nitrate 56, woodmeal 13 and chalk 1% (Ref 2). It can also be used as a substitute for Tetranitroglycerin, Nitroglycerol (NGk), Glycerinchlorohydryn dinitrate, and Nitrosgars. NIBGkDN can also be used in conjunction with NC to form gelatinized expls, or with various oxidizers such as K nitrate, AP, AN, etc, in the prepn of Dynamites
References: 1) Beil – not found 2) F.H. Bergeim, USP 1691955 (1929) & CA 23, 708 (1929) 3) W.deC. Crater, USP 2112749 (1938) & CA 32, 3964 (1938)

Nitrocellulose. Fr for Nitrocurds. See in Vol 3, C577-L
**Nitrocarbamates.** Salts of Nitrocarbamic Acid. See under Carbamic Acid and Derivatives in Vol 2, C40-Lff.

**Nitrocarbamic Acid.** See under Carbamic Acid and Derivatives in Vol 2, C40-Lff.

**Nitrocarbol.** Same as Nitromethane. See under Methane and Derivatives in this Vol.

**Nitro-Carbonitrate (NCN) Blasting Agents.** This term has been employed for US federal regulatory purposes to cover and to group a class of competitive (various trade-named) explosive products, less sensitive than Dynamites, employed in blasting operations around quarries and open-pit mines. It covers essentially any materials or mixts consisting of a fuel and oxidizer (substantially inorganic nitrates) combination in which none of the materials are considered to be explosives under the usual definition. This class includes among its products any Amm nitrate preparations sensitized with some form of combustible, usually carbonaceous. These include carbon black, powdered coal, sawdust, sugar, molasses, and more generally, No 2 diesel or home heating fuel oil.

All NCN blasting agents and each of their components must be cap-insensitive, i.e., incapable of being detonated when initiated by a No 8 blasting cap. Both Nitro-Carbonitrates and Amm nitrate are grouped by the ICC as “oxidizing materials” with normal transportation (yellow label) being permitted (Ref 1).

The chief advantages in NCN blasting agent use are related to economy, efficiency and safety. In certain applications, an overall cost saving of up to 75% over conventional NG expls has been reported. Where used under well-controlled conditions, it is reported to perform as well as or better than Dynamites, and, by virtue of its greater gas production, may even give better fragmentation. It is safer to handle and use because its hazard sensitivity is low, and misfires are easily and safely resolved. One of its important virtues is that it is not classified as an explosive; but when mixed in the correct stoichiometric proportions under preferred physical conditions with adequate priming, the mixt becomes a powerful low-cost explosive (Ref 5).

See also under Blasting Explosives in Vol 2, B202-L to B211-R.


**Nitrocellulose.** See under Cellulose Nitrates in Vol 2, C100-Lff.

**Nitrochlorbenzenes.** See under Chlorobenzene and Derivatives in Vol 3, C248-R to C251-R.

**Nitrochlorin.** Low-freezing expl oil used in the manuf of some Dynamites. It consisted of Dinitrochlorohydrox 80 and NG 20%.

Ref: 1) Naoum, Expls (1927), 113 2) PATR 2510 (1958), Ger 119-R.

**Nitrochloroform.** See under Chloroform and Derivatives in Vol 3, C256-R.

**Nitrocoal.** See under Coal, Nitrated in Vol 3, C378-L.

**Nitrocolle.** Fr for Nitratred Glue. See in Vol 6, G85-L.

**Nitrocolophony.** Fr for Nitrorosin.

**Nitrocooper.** $\text{Cu}_2\text{NO}_2$. A compd corresponding to this formula was prepd in 1892 by the action of nitrogen peroxide ($\text{N}_2\text{O}_4$) on cuprous oxide at room temp. Up to 30% by wt of $\text{Cu}_2\text{O}$ reacted without change of appearance of the solid compd. When heated in the absence of air, the
nitrogen peroxide was liberated, leaving Cu₂O. This indicated that the peroxide was absorbed and did not react chemically. The N₂O₄ could also be removed by placing Nitrocellulose in an inert solvent such as CCl₄ at 65–70°. When placed in water, a violent reaction occurred, with formation of NO, Cu(NO₃)₂, and some Cu(NO₂)₂.

Ref: Thorpe 8 (1947), 527

**Nitrocotton.** A NC prep'd by nitration of cotton. See under Cellulose and Derivatives in Vol 2, C95-Rff

**Nitrocresols.** See under Cresol and Derivatives in Vol 3, C556-R to C558-L

**Nitrocresol sulfonic Acid Explosives.** See under Cresol sulfonic Acid and Derivatives in Vol 3, C558-L

**Nitrocresyl resins.** Salts of Trinitrocresol. See in Vol 3, C557-R

**Nitrocumenes.** See under Nitro Derivatives of Cumene in Vol 3, C573-R to C574-R

**Nitrocurs.** See under Curds in Vol 3, C577-L

**Nitrocymanes.** See in Vol 3, C637

**Nitrodextrin.** See in Vol 5, D1115-R

**Nitrodiazonaphthol.** See under Diazonaphthol and Derivatives in Vol 5, D1168-R to D1169-R

**Nitrodiazophenol.** See under Diazophenol and Derivatives in Vol 5, D1172-L

**6-Nitro-4-Diazotoluene-3-Sulfonic Acid (p-Nitrodiazotoluenesulfonic Acid).** H₃C₆H₄(NO₂)(SO₃)₂N₂, mw 243.20, N 17.28%, OB to CO₂ -75.7%, brown prisms; mp, expls on heating, as low as 75°, without melting.

Can be prep'd by diazotization of 6-nitro-4-aminotoluene-3-sulfonic acid with K nitrite and dil sulfuric acid. It has also been isolated by Batik (Ref 2) from the wash wth the sulfite purification of TNT. It was assumed that the following reaction takes place:

\[
\text{O}_2\text{N} \begin{array}{c} \text{CH}_3 \\ \text{NO}_2 \end{array} + \text{Na}_2\text{SO}_3 \rightarrow \text{O}_2\text{N} \begin{array}{c} \text{CH}_3 \\ \text{SO}_3\text{Na} \end{array} + \text{NaNO}_2
\]

On acidification of the waste w, there is formation of sulfurous acid (from excess Na₂SO₃) and nitrous acid (from the NaNO₂). The former reduces the NO₂ group in the 4-position to NH₂ and then the latter diazotizes it.

P-Nitrodiazotoluene sulfonic acid is insol in w and alc. It is an expl, which may be stored in a dry state. It expls on heating, but not on impact.

**Note:** One reason why TNT waste w should not be acidified is the possible formation of this expl compd.

Ref: 1) Beil 16, 568 2) B. Batik, Chem&Ind Spec No 960-3 (June 1933) & CA 28, 645 (1934)

**1-Nitro-5,5-dimethylhydantoin.** See under Dimethylhydantoin and Derivatives in Vol 5, D1343-R

**2-Nitro-2-(3',5'-dinitrophenyl)-propanediol-1,3.** (O₂N)₂C₆H₃C(NO₂)(CH₂OH)₂, mw 287.19, mp 124.6–125.3°, colorl needles.

Can be prep'd, according to Fieser and Gates (Ref 2, p 2251) by adding 1 ml of triethylamine to a mixt of 10g of 3,5-dinitrophenylnitromethane (prep'd by Urbański's method, Ref 1), 10ml of formalin, and 40ml of dioxane. After heating to 60°, the resulting brownish oil was treated with benz (after removing the dioxane) to extract the nitrodinitrophenylpropanediol, which was then crystd twice from benz contg a little acet. The yield was about 69%.

On nitration, it gives an expl dinitrate (see below)
2-Nitro-2-(3',5'-dinitrophenyl)-propanediol-1,3 Dinitrate. \((\text{O}_2\text{N})_2\text{C}_9\text{H}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{ONO}_2)\), mw 377.19, N 18.57%, OB to CO₂ -40.3%; colorl, flat, rectangular plates from alc contg a little acet, sometimes occurs in the form of prisms; mp 115.2-115.8°. Sol in acet and sl sol in alc.

Can be prep'd in the following manner:
Add 20.0g of 2-nitro-2-(3',5'-dinitrophenyl)-propanediol-1,3 in several portions to 130ml of fuming nitric acid (d 1.5g/cc) cooled to 5°. After about 6 minutes all of the material is dissolved and the temp rises to 10°. Drown the mixt in 1.5l of ice w and allow it to stand for 15 minutes. Collect the hardened, gummy material and w wash. Purify by dissolving in acet and crystg by adding alc to the so1. The yield varies between 67 and 86%. 

Notes: 1) Nitration with mixed nitric-sulfuric acid gives a less satisfactory product and a lower yield (about 52%). 2) Attempts to prepare the product starting with 2-nitro-2-(m-nitrophenyl)-propanediol-1,3 or its dinitrate were unsuccessful. Its expl props were detd by R. McGill et al at the NDRC Res Lab at Bruceton, Pa and were found to be as follows:

**Ballistic strength.** 126% of TNT, 125.5% of Tetryl, 145.8% of PETN and 150.2% of RDX

**Impact sensitivity.** slightly less than PETN

**Refs:** 1) T. Ubraniński, CR 206, 1122 (1938)
2) L.F. Fieser & M. Gates, JACS 68, 2249-52 (1946) & CA 41, 733 (1947)

**Nitrofulminite (Nitrofulcitol).** See under Dulcitol and Derivatives in Vol 5, D1567-R

**Nitroerythrite.** Same as Erythritol Tetrinitrate; see in Vol 5, E124-L to E125-L

**Nitroethanes.** See under Ethane, Nitrated and Nitrosated Derivatives in Vol 6, E143-Rff

**Nitroethanols.** See in Vol 6, E177-Rff

**Nitroethylenes.** See in Vol 6, E229-Lff

**Nitroform.** Same as Trinitromethane; see under Methane and Derivatives in this Vol

**Nitrogalactose.** See under D-Galactose and Derivatives in Vol 6, G8-L

**Nitrogelatines.** Fr term for Blasting Gelatin. Other terms include Gélatine Dynamite, Gélatine Explosive, Gélatine, Dynamite-Gélatine, etc

**Ref:** Daniel (1902), 325 & 523

**Nitrogélatine Pierique.** A mixt patented in 1887 by the Deutsche Sprengstoffe Gesellschaft, which consisted of NG plus NC jelly, mixed with about 10% Picric Acid. It proved to be unstable

**Refs:** 1) Daniel (1902), 523 2) PATR 2510 (1958), Ger 119-R

**Nitrogelatinendynamiten.** Swiss for gelatine-dynamites containing 20-25% NG (or a low-freezing mixt of 4/1 NG/Nitroglycerol) gelatinized with collodion cotton, AN and a liq aromatic nitrocompound (such as drip oil, called "flüssiges Tri", which is a mixt of crude DNT and TNT) serving as a phlegmatizer. These expls, among them Alderfit, Gamsit and Telsit, belong to the class of so-called "Sicherheitsdynamite", which are safe to handle and transport (Handhabungssichere), and safe to use in coal mines

**Ref:** Stettbacher (1948), 86

**Nitrogen Determination in Energetic Materials**

The element Nitrogen can exist in the uncombined or free state, as in the atm or in natural gas, or in a combined or bound state,
as in nitric acid, ammonia, amines, nitrates, nitric esters, azides, cyanides, aliphatic and aromatic nitrocompds, etc.

The analysis of free nitrogen in gas mixts can usually be caled by difference after detg the concn of the other gaseous ingredients. The presence of free N₂ can be detected by spectrographic (Refs 55 & 60) or colorimetric techniques (See Vol 1, A114-R & Refs 9 & 17). The element can be quantitatively detd by these means or thru the use of mass spectrometry (See in this Vol & Refs 52, 53, 55 & 61).

The qualitative determination of combined nitrogen in energetic materials can be performed using a variety of tests. For salts of ammonia, treatment with Nessler's reagent yields a yellowish-brown coloration or brown ppt (See Vol 3, C406-R & Ref 17). If nitrogen is present as either nitric acid or nitrate (such as KNO₃, NaN₃, NH₄NO₃, NG, NGC, etc) a ring test using either diphenylamine (blue ring) or ferrous ammonium sulfate (brown ring) can be used (See Vol 3, C405-R & Ref 17). The presence of azides can be detected using FeCl₃ reagent (See Vol 1, A617-L & R). Several methods for detecting nitrates are available. One procedure, Ilosvay's method, uses sulfanilic acid which yields a red, fuchsia-like coloration (See Vol 3, C406-R & Ref 17). Another procedure, using K permanganate, can also be used quantitatively. If the red color of this reagent disappears there is a possibility of nitrite presence (Ref 17). Detection of a nitrate in the presence of a nitrite can be accomplished using an I₂O₃ soln in sulfuric acid. A blue color is developed (Ref 17).

For a complete description of color reactions and reagents used for the detection of over 75 expls and proplnts see Vol 3, C405-L to C420-L. Additionally, a technique has been developed for the detection of combined nitrogen in microgram samples thrpu the use of a chelating complex of Zn-8 quinolinol. The complex-nitrogen adduct exhibits intense greenish-yellow fluorescence under ultraviolet light (Ref 25). Also, the use of infrared spectroscopy to identify bound nitrogen groups, and hence their compounds, is another widely used qualitative method (See Vol 7, 1100-R to 1101-R & Ref 61).

The quantitative detn of combined nitrogen in energetic materials is of the greatest interest and importance. Of the many procedures to be found in the literature, only the most important and useful will be addressed here (See Vol 1, A369, A400-R & A474; Vol 6, E483 to E488).

Chromatography in its various forms (thinline, column, gas, gas-liq, & electrophoresis) is frequently used to separate and detn NG, NGC, Nitrosamines, Nitramines, etc. In this technique, microgram quantities of a sample are added to a column packed with an absorbing medium or phase. Over this is maintained a flow of mobile phase (gas or liq). The sample components separate because of their relative mobility in the absorbing phase and thus leave the column at different times (See Vol 1, A177-R; Vol 2, C46-L; Vol 3, C289-L to C298-L [Chromatography]; Vol 5, D1344-R & D1643-R; Vol 6, G107-L; Vol 7, H97 & Refs 45, 48, 49, 50, 55, 56 & 58).

One of the most widely used techniques for the detn of nitrogen content involves the decompn of the sample with subsequent measurement of the evolved nitrogen gas over mercury in a nitrometer, ozometer, eudiometer, Schultze-Tieman app, etc. This method is a standard one employed in many energetic material Specs (See Vol 1, A373-L to A378-R; Vol 2, C119-R; Vol 6, E267-G105; Vol 7, L61-R & Refs 4, 16, 17, 21, 38, 43, 54, 56, 57, 61 & 62).

An often used method for the detn of either aminoid or nitrate nitrogen is the decompn-volumetric Kjeldahl (or Chenel) procedure in which the sample is decomp with concd sulfuric acid and suitable catalyzer to yield amm sulfate quant. After release with strong alkali, the ammonia is quant distd into an excess of standard acid and back-titrated with standard alkali (See Vol 1, A616-R; Vol 2, C46-L & C50-L; Vol 3, C276-L & C357-R; & Refs 4, 17, 32, 33, 38, 47 & 63).

Polarography, a well known electroanalytical technique, is currently being used to detn the purity of Tetracene as well as other compds contg nitrate and nitroso groups (Ref 38).

This technique involves gradually increasing the potential applied to a micro electrode immersed in a soln of inert electrolyte contg a small quan of an electroactive species. While the potential is gradually increased, the associated increase in diffusion current is monitored. An X-axis asymp-
The primary change in the current curve indicates the end-point of the analysis (see Vol 6, G161-R & Refs 20, 34, 38, 41 & 161)

A universal procedure for combined nitrogen is the Dumas method. This gasometric procedure is applicable to any organic compound containing nitrogen in any form, such as amino, nitroso, nitro, azo, cyano, nitrate, nitrite, as well as N in heterocyclic compounds. The procedure involves combusting the sample in a closed system in a CO₂ stream, with subsequent reduction of the oxides of nitrogen to N₂ which is collected quantitatively in a nitrometer (see Vol 1, A418-R; Vol 6, G172-L; & Refs 4, 17, 27, 28, 42, 47, 61 & 163).

Gravimetric methods applicable to energetic materials include the determination of NH₄ in AN using chloroplatinic acid (Ref 17); for nitrates using Nitron (Refs 15 & 17) or the di-cyclohexyl Tl⁺ ion (Ref 29); for nitrites using Ag nitrate (Refs 2 & 17); and for the thiocyanate ion using Ag nitrate (Vol 4, D1065-L).

There are two important hydrogenation (or reduction) titration procedures for the determination of N as ammonia. The Devarda method involves the quantification of nitrates to ammonia in alkaline solution using an Al-Cu-Zn alloy. The ammonia evolved is distilled into standard sulfuric acid and titrated. This procedure is used for K nitrate, nitric acid, nitrites, or ammonia (see Vol 6, G107-L & Refs 3, 4, 14, 17, 19, 31, 34, 43 & 47). Another procedure, the Ter-Meulen hydrogenation method, consists of heating nitrate, nitrite, or nitroso compounds at about 350°C in the presence of finely divided Ni, absorbing the ammonia formed in standard acid and titrating with standard alkaline solution (Refs 4, 5, 6, 7, 8, 10, 12, 13, 17 & 47).

One of the least expensive and popular techniques for the quantitative determination of N in energetic materials is that of titrimetry. There are currently three basic titrimetry systems used: acid-base, redox, and non-aqueous (involving both acid-base and redox systems in which there is association, not ionization of the reactants). The simple acid-base titrimetry system has been shown, earlier in the article, being used in the Kjeldahl, Devarda and Ter-Meulen procedures to determine liberated NH₃. It is also utilized, for example, to determine nitrosylsulfuric acid in mixed acids, total acidity in nitric acid, NG in Aexp oils, and the N content of ethyldiethanolamine (see Vol 1, A88-Rf & A304-L; Vol 2, C138-R; Vol 3, C276-L; Vol 5, D1640-Rf; Vol 6, E226, E266 & G107-L; & Refs 3, 17, 18, 38, 40 & 62).

Redox (reduction-oxidation) titrimetry is used primarily for nitrate detms. Five systems are in current use: ferrous sulfate-dichromate, iodometric, periodic acid oxidation (NaOH titrant), K permanganate, and titanium chloride-ferric ammonium sulfate. The ferrous sulfate-dichromate system is used for MNT & DNT detms (Vol 2, C162-Lf; Vol 6, F17-Rf & Ref 17). In the iodometric procedure, the sample (i.e., NG) is treated in a CO₂ atm with a saturated solution of Mn chloride in concd HCl, the vol reaction products are bubbled thru a K iodide soln, and the liberated iodine is titrated with standard thiosulfate soln (Refs 1 & 17). The periodic acid oxidation procedure is used to detn NG in Aexp oils (Vol 5, D1640-R to D1641-R). The NO₂ content of nitric acid is detd with standard K permanganate soln (Vol 1, A88-R to A89-L & Refs 17, 29 & 54), while the titanous chloride-ferric ammonium sulfate system is primarily employed to detn nitro groups and nitrates in such energetic materials as NG, TNT, RDX, LST, NGU, nitrobenzenes and nitroanilines (see Vol 1, A415-R, A418-L to A419-L & A458-R; Vol 2, C50-L; Vol 3, C251-R, C474-R, C476 & C540-L to C541-L; Vol 5, D1272-R, D1282-L to D1283-R & D1646-L to D1648-R; Vol 6, E211, F17-R to F19-L, G106-R to G107-L, G160-R to G161-L & G163; & Refs 17, 22, 35, 37, 38, 39 & 54).

Nonaqueous titrimetry has been applied to the detn of nitroaromatic nitrate, nitrates, RDX, 4-nitroanisole, Tetryl, Haleite, TNC, K nitrate in M-8 propellant and NGU (see Vol 1, A165-R; Vol 3, D102-L & C625-R to C626-L; Vol 6, G154-L & G161; & Refs 30, 30a, 30b, 30c, 30d, 30e, 30f, 30g, 35, 59 & 61).

The widely used technique of light spectroscopy has also been applied to the qualitative and quantitative determination of bound N in energetic materials. There are five distinct systems used: colorimetry, infrared spectroscopy, polarimetry, Raman spectroscopy, and ultraviolet spectroscopy.

Colorimetry is employed to the detn of the primary materials as Na Azide and DPA. The method depends on the formation of a colored complex between the bound N group and a me-
tallic ion such as ferric or ferrous (Vol 1, A303-L & A617; Vol 6, F18-L; & Refs 9, 11, 17, 38, 39, 54 & 63).

Infrared spectroscopy is used not only to identify functional N containing groups, but to quantify the amount of nitrogen present in the sample. Procedures have been developed for nitrate, nitrite, nitrites, the determination of EGDN in the presence of EG, and for Anisele & alkyl derivatives (Vol 1, A455-L; Vol 6, E270-L to E278-R, Vol 7, I100-R to I101; & Refs 36a, 46, 54, 61 & 63).

Polarimetry, in which a beam of polarized light is rotated by passage through an optically active substance, has been applied to the quantitative analysis of sucrose octanitrate (Vol 5, D1643-R & Ref 61).

Raman spectroscopy has been utilized in the quantification of nitramines and nitroamines (Vol 1, A177-R & Ref 61), and ultra-violet spectroscopy is employed for the quantitative measurement of TNT in HBX compn (Ref 39, 61 & 63).

A modern technique for nitrogen detection is known as fast neutron activation analysis. Materials such as RDX are exposed to a high density fast neutron flux which converts the non-nitrogen-containing sample into unstable 13N. The N is detected by measuring the 13N produced by the 14N(n, 2n) 13N reaction. This technique is extremely sensitive, but requires specialized instrumentation (Refs 44, 51 & 61).

Written by H. L. HERMAN


Nitrogen Bromide. See under Nitrogen-Halogen Compounds in this Vol

Nitrogen Chloride. See under Nitrogen-Halogen Compounds in this Vol

Nitrogen Dioxide. See under Nitrogen Oxides in this Vol

Nitrogen Fluoride. See under Nitrogen-Halogen Compounds in this Vol

NITROGEN-HALOGEN COMPOUNDS

Nitrogen Bromides

Bromamide (Bromamine). BrNH₂, mw 95.93, N 14.6%; the solid is purple-black when unsolvated, yellow when solvated, and yellow in soln (Refs 4 & 6); mp decomp's violently above -80° with evolution of Br (Ref 4). In w there is a UV absorption peak at 277µm, and in eth at 275µm, the w peak being more prominent than the peak in eth (Ref 5); CA Registry No 14519-10-9. It was first prepd by the action of Br on liq ammonia which gave a mixt of bromamide and N tribromide solvated with 6 moles of ammonia (see below) (Ref 1). It has also been prepd, along with some bromamide, by the action of Br on ammonia in eth at -80° (Ref 2); in dil aq soln by the action of Br on aq ammonia (Ref 5); and in the vapor phase by the use of an app similar to that used by Sisler to prep chloramine (see above) (Ref 8); yield is low. It can be pptd from eth at -80° by the addn of pentane (Ref 6), and can be identified in aq soln by the ad- duct it forms with triphenylphosphine, (H₂NPPh₃Br⁺), mp 247-9° (Ref 8). Recent work has shown that bromamide can be stabilized in w by an excess of ammonia (Ref 7)

Bromimide (Dibromamine). Br₂NH, mw 174.82, N 8.01%; in w there is a small UV peak at 235µm with a broad shoulder at 270-90µm (Ref 5); CA Registry No 14519-03-0

It is prepd by the action of Br on ammonia in eth soln (Ref 3), or on liq ammonia (Ref 5). It is stabilised in aq soln by an excess of ammonia (Ref 9)

Nitrogen Tribromide, NBr₃, mw 235.72, N 5.5%; its UV spectrum in w has a peak at 227µm, and in chl at 267µm (Ref 5); CA Registry No 15162-90-0

It is prepd by the action of Br on ammonia in w (Ref 5), or on liq ammonia (Ref 1). It is stabilized in aq soln by an excess of Br (Ref 9). The kinetics of the decompn of N tribromide in aq soln were studied. It was found that at a pH of 7 and an ammonia concn of 6.6x10⁻⁵M, the 2nd order decompn constant was 4.1%/mole sec (Ref 10).

NITROGEN CHLORIDES

Chloramine (Chloramide, Monochloramine).
ClNH₂, mw 51.48, N 27.2%; a colorless liq or crystals, mp -66°, decomps above the mp (Refs 2 & 8). It has an IR absorption peak at 2430Å which can be used for spectrophotometric analysis (Ref 3). It is unstable at room temp except in aq soln, so it is stored and handled in this form (Ref 4); CA Registry No 10599-90-3

It has been prepd by various proc using chlorinating agents, ie, Cl₂ gas or hypochlorites in aq or anhyd ammonia. For example, the interaction of Cl₂:ammonia:N 1:2.04:12.73 at 300° in a flow reactor gives chloramine which is absorbed in a suitable solv at 75° (Ref 9). An app is described in Ref 10 for the improved prep of chloramine using a Cl₂:ammonia:N ratio of 1:8.6:3.2, max yield 95%. It has also been prepd by the hydrolysis of N₂,N₂-dichloro-
urea (Ref 1)

Uses: It is one active ingredient present in water which has been purified by chlorination (Ref 6). It is used as an intermediate for the prep of hydrazine and substituted hydrazines. Recently there has been a renewed interest in chloramine as a possible intermediate for the prep of UDMH (see Vol 7, H203-R) which avoids handling the highly carcinogenic dimethyl-
nitrosoamine (Refs 5 & 7)


Dichloramine (Dichloramide, Chlorimide).
Cl₂NH, mw 85.92, N 16.3%; CA Registry No 3400-09-7

Chlorimide is an unstable gas which can be stored in aq soln; the pure gas decomps within 7 min (Ref 2). It is the least stable of the chloramines (Refs 3 & 5). It is best prepd by the interaction of Cl and Amm salts in w at a pH betw 4.4 and 8.5 (Ref 1). The IR spectrum of mixts of chloramines is given in Ref 2. It is one of the active species present when w contg Amm salts or amines is purified with Cl (Ref 4)


Nitrogen Trichloride. NCl₃, mw 120.38, N 11.63%; a dense yel liq, mp -27°, bp (extrapolated) 71° (Ref 8); Q₁ in C tetrachloride -55.0 kcal/mole (Ref 5); CA Registry No 10025-85-1

The expl nature of N trichloride has been known since the end of the 18th century when Sir H. Davy reported, "The fulminating oil which you mentionedroused my curiosity and nearly deprived me of an eye. After some months confinement I am again well." (Ref 12). The early history of this compd is reviewed in this Ref. It is readily prepd by the action of Cl on ammonia or Amm salts (Refs 2, 6 & 13); or by the electrolysis of an unstirred concd soln of Amm chloride at 35-40° (Ref 4). A procedure for the prep of a soln of N trichloride in clhf is described in Ref 1, and prepn on an industrial scale in Ref 7

Explosive Properties. It is a sensitive and powerful expl (Ref 9). Mixts of N trichloride, H, & Cl expld with a bright flash (Ref 10). It also explds violently on heating, exposure to light, or on contact with org compds (Ref 8); Q₆ ca -55 kcal/mole (Ref 11)

Uses: It is one active species present when w contg Amm salts or amines is purified by chlori-

Refs: 1) W.A. Noyes, JACS 60, 2904 (1928) 2) J.G.A. Griffiths & R.G.W. Norrish, TrFarad-
Chlorine Azide (Trinitrogen Chloride). $\text{CIN}_3$, mw 77.47, N 54.2%; an orange-yel liq or orange solid, mp ca. $-100^\circ$, bp ca. $-15^\circ$ (Refs 2 & 5). It is extremely sens and can expld without provocation at any time, but can be stored indefinitely at low temp in sealed ampules when shielded from light (Ref 2). Its UV and visible spectra are in Ref 6.

It has been prepd by the action of Cl on Ag azide in eth (Ref 1), or better by the addn of acet ac to a mixt of Na azide and Na hypochlorite (Ref 2). The expln limits of mixts of gaseous Cl azide with Ar, N, and C dioxide are in Ref 3. The shock wave formed by the expansion of the gas into a vacuum is sufficient to cause decompn (Ref 5), $Q_e -93.2 \pm 1.5$ kcal/mole, flame temp at 20mm 3380$^\circ$K (Ref 6). Mixts of Cl azide: N trifluoride: H 1:1:2 at 12–24 torr are initiated with a Xe flash lamp to produce explns which excite a H fluoride laser. Cl azide, S hexafluoride, H mixts were similarly used (Ref 7).


It has been prepd by the action of phosgene or H chloride on fluorimide (Ref 3); by the action of F diluted with N on a mixt of Na azide and Na chloride (Ref 1); by the action of Cl on fluorimide in the presence of Na fluoride (Ref 4); in 68% yield by the action of Cl on the addt of trifluoroformamide ($\text{F}_2\text{NCOF}$) with K fluoride in perfluoracetone (Ref 6); or by the photolysis of a mixt of tetrafluorohydrazine and thionyl chloride (Ref 8).

It decomp slowly when stored in metal cylinders (Ref 5). Its expl props have not been examined.

Dichlorofluoramine, $\text{FNCI}_2$, mw 103.91, N 13.5%; a gas, bp $-3 -2^\circ$ (Refs 2 & 7); CA Registry No 17417-38-8

It is prepd by the action of Cl monofluoride on Na azide, yield 20% (Ref 2), $Q_e -90.1\pm2.9$ kcal/mole, flame temp 3350$^\circ$K (Ref 3). Mixts of N trifluoride: Cl 1:1:2 at 12–24 torr are initiated with a Xe flash lamp to produce explns which excite a H fluoride laser. Cl azide, S hexafluoride, H mixts were similarly used (Ref 7).


NITROGEN FLUORIDES

Inorganic Compounds, compounds derived from ammonia

Fluoramine (Nitrogen Dihydrogen Fluoride, Amine Fluoride). $\text{FNH}_2$, mw 35.62, N 39.32%; a colorl gas, subl $-77^\circ$ and 760mm (Refs 3 & 4); CA Registry No 15861-05-9. The isolation of fluoramine was first claimed by Ruff & Staub who isolated it in low yield by the electrolysis of molten Amm fluoride (Ref 1). They reported it to be an expl gas which has a distinctive odor and is very toxic (Refs 1 & 2). More recently it was found that fluoramine could be conveniently prepd by the acid hydrolysis of $N$-fluorourethan, and that the mat isolated by Ruff & Staub was probably impure (Ref 5).
Salts, Methanesulfonate, FNH₃⁺MeSO₃⁻, mp 103–05⁰ with decmpn; CA Registry No 20175-02-4. It is prepd by the reaction of N-fluorourethane (FNHCOCEt) with methanesulfonic acid in chlf (Ref 5).

Perchlorate, FN₃⁺ClO₄⁻, mp 104–05⁰ with decmpn; prepd by addn of N-iso-Pr-N-fluorourethane to a soln of perchloric acid in chlf (work must be done behind a good safety shield as compds are expl) (Ref 5).

Trifluoromethanesulfonate, FNH₃⁺CF₃SO₃⁻, mp subl; CA Registry No 42138-65-5. It is prepd by the reaction of N-fluorourethane with trifluoromethanesulfonic acid in methyl chloride (Ref 6). It is more stable than the salts listed above (Ref 6), and upon subln at low press, it dissociates into fluoramine and trifluoromethanesulfonic acid without decmpn (Ref 7).


Difluoramine (Fluorimide, Fluorimine). HNF₂, mW 63.02, N 22.23%; a colorl gas, mp -116-3⁰, bp -23.6⁰ (Refs 4 & 6), crit temp 130⁰ (Ref 5), vapor d 1.424 -0.00202t (Ref 6), an odor resembling H cyanide, and is extremely toxic (Ref 1); CA Registry No 10405-27-3. The first prepn of difluoramine was claimed by Ruff & Staub who claimed to have obtained it in low yield by the electrolysis of molten Amm bifluoride (Ref 1), although more recent work indicates their prod was impure (see below).

More recent preps are by the reaction of tetrafluorohydrazine (F₂NNF₂) with thiophenol, yield up to 74% (Ref 7); by treatment of triphenylmethylfluoramine with sulfuric acid, yield almost quant, purity by mass spec 99% (Ref 10); and by fluorination of: 1) cyanuric acid (Ref 5); 2) sulfamide, yield 45% (Ref 14) [Kelly and Sukornick found that sulfamic acid, w, and F will react contnously in a flow reac. to generate difluoramine in 77% yield based on F consumed (Ref 15)]; or 3) urea, yield 15% (Ref 6). Exptl details of the prepn from urea are given in Ref 9, and further exptl details including necessary precautions are given in Ref 20. Its purification is difficult (Ref 2) and is best done in a high vacuum system by trap-to-trap distn (Ref 7).

Hazard. Solid difluoramine, upon warming from liq N temp to its mp, can detonate without warning (Ref 13); the pure compd in the solid or liq state can detonate at any time without warning (Ref 5); and it can expl on contact with air (Ref 7). Above 100⁰ it decomps explosively (Ref 3). It can be stored indefinitely in glass (Ref 5), and is best handled and stored as an aq soln (Ref 5).

Thermochemical Data. In the ideal gas state at 1 atm and from 200 to 2000⁰K the following values were obtained: entropy 51.731-84.336, heat capacity 8.937–18.717, heat content 8.182–15.238, and free energy 43.549–69.998 kcal/mole (Ref 8); Qₑgₐₐ₃ -15.6, Qₑq₂ₚₐ₉ₐ₃ -22±1.5 kcal/mole (Ref 19); Qᵥ 5940 cal/g (Ref 16).

Specrum. IR spectrum is in Ref 11 and the mass spectrum cracking pattern is in Ref 5.

Thermal Decomposition. It decomps in the gas phase at 275⁰ in Teflon or Monel to give N, H fluoride, and tetrafluorohydrazine (Ref 21).

Reactions. It reacts with an aq soln of low pH to form difluorodiazine (FN,NF) and nitrous oxide, and with Fe⁴⁺ to form tetrafluoro hydrazine in good yield (Ref 13). It reacts with carbonyl compds under mild conditions to give alpha-difluoramino alcohols (Ref 18); and under vigorous consds, ie in presence of concd sulfuric acid, to give gem(bisdifluoramino) compds; and with 2,3-unsaturated carbonyl compds to give (F₂N)₂C₂H₂CHN (Ref 17).

Uses. Its primary use is in the prepn of organic difluoramino compds. A 1:1 adduct of difluoramine with methyl ether can be used as a rocket propilt, lsp 229sec at 1000psia. In the range difluoramine:methyl ether 4–8:1 the lsp is 282–93sec; and in the range difluoramine: ether 5–8:1 the lsp is 283–92sec; other ethers can be used (Ref 12).

Refs: 1) O. Ruff & L. Staub, ZAnorgChem 198, 32 (1931) & CA 25, 5105 (1931) 2) O. Ruff,

Difluorodiazine (Dinitrogen Difluoride). N2F2, mw 66.02, N 42.4%; a colorless gas, freezes to lustrous transparent cubic crystals, odor similar to N dioxide (Ref 1); bp -110° (Ref 1); CA Registry No 10578-16-2

It is prepd by the thermal decomp of F azide (Ref 1); as a by-prod from the fluorination of Amm bifluoride (Ref 2); by the photolysis of tetrafluorohydrazine at room temp (Ref 4); or by the fluorination of Na azide (probably thru F azide followed by decomp)(Ref 6)

The crude compd can be fractionated into two isomers:
cis-Difluorodiazine (Z-Difluorodiazine). FN

mp below -195°, bp -105.7° (Ref 2); Qv 3670cal/mole, crit temp -1° (Ref 2), Qr at bp 20.5±2.0kcal/mole (Ref 5); CA Registry No 13812-43-6

trans-Difluorodiazine (E-Difluorodiazine). NF

mp -172°, bp -111.4° (Ref 2); Qv 3400cal/mole, crit temp -13° (Ref 2); CA Registry No 13776-62-0

It has been proposed that the higher boiling, more reactive isomer is F2N:N (Ref 3), but more recently, electron diffraction studies have confirmed that the two isomers are cis and trans forms (Ref 7). Both isomers react with Hg and can explod on contact with org mat. Stopcocks and valves of vac app should be lubricated with silicone grease (Ref 2)


Nitrogen Trifluoride. NF3, mw 71.01, N 18.67%; a colorless gas, mp -206.71° (Refs 4 & 7), bp -129.01°, triple point 66.361 ± .373°K (Ref 3); CA Registry No 7783-54-2

It was first prepd by the electrolysis of fused Amm bifluoride (Ref 1) and later by sparking a mixt of F and N at liq N temp, yield 30% (Ref 11). It is now being prepd commercially by the former proc (Ref 12)

Explosive Properties. N trifluoride is the most stable of the N halides, but it can detonate in the presence of hydrazoic acid (Ref 13) or org compds (Ref 10). Ozone, which is one by-prod of the electrolysis of Amm bifluoride, was found by Ruff and coworkers to cause violent explosns in the reaction vessels and gas lines. They found that the ozone could be removed by passing the off-gas thru pyrosulfite, thus reducing considerably the expln hazard (Ref 1). It also decompds explosively above 100° (Ref 2)

Flammability. The flammability limits of mixts of N trifluoride with gaseous fuels and the effect of N as a diluent are given in graphic form in Ref 18. Fuels examined are H, butane, and hexafluoroethane. The authors also report that
the flame vel of N trifluoride/hydrocarbon mixts is 3 times that of O/hydrocarbon mixts, hence the danger of fire and expn with N trifluoride is much greater than with O mixts. They also concluded that the fire hazard of N trifluoride is much greater at elevated temps and that it will ignite most materials if the temp is high enough (Ref 18). By diluting the gas or liq to below 9.4 mole % with an inert mat such as N, the expn hazard can be almost eliminated (Ref 12)

**Spectrum.** The IR spectrum is in Ref 17

**Thermodynamic Properties.** Energy of N–F bond 61.1 kcal/mole (Ref 15); Q^238 = 31.440 kcal/mole (Ref 17)

**Toxicity.** A 1% concn of the gas in air is lethal to rats in 1 hour, its effect being similar to C monoxide; the LD50 in rats when injected intraperitoneally is 8.2 ml/kg (Ref 16). Earlier workers assumed that the toxicity of N trifluoride would be similar to H fluoride and that the latter would be formed by hydrolysis in body tissues (Ref 1). This has recently been shown to be erroneous, and that it is stable under physiological conds. The toxic effect is due to its ability to complex with the hemoglobin of the blood causing anoxia. This effect is reversible, and animals receiving a sublethal dose recover rapidly upon removal from contact with N trifluoride (Ref 14)

**Uses.** A review of its use as an oxidizer in rocket propmts is given in Ref 6. A 50:50 mixt of N trifluoride:F, with ammonia as fuel, yields a specific impulse of 295 sec and a d impulse (specific impulse X d) of 340 (Ref 6). Mixts with methyl fluoride, 1,1-difluoro propane, and 1,3-difluoropropane have been patented as monopropnts (Ref 9). A N trifluoride/H flame has been proposed as a cutting and welding torch (Ref 8)


**Tetrafluoroammonium Salts**

**Tetrafluoroammonium Hexafluor arsenate**, NF$_4^+$ AsF$_6^-$, mw 278.95, a white solid, decomps ca 175° (rapid heating) into N trifluoride, As pentfluoride, and F (Ref 8); CA Registry No 16871-75-3

It is prepd by heating a mixt of N trifluoride, As pentfluoride, and F in a Monel tube reactor at 200° for 2–5 days (Ref 1); or by passage of the same reagents thru a glow discharge (Ref 4). Differential thermal analysis indicates that on slow heating the decomp starts ca 270° (Ref 2). Its IR and NMR spectra are given in Ref 3. It is a useful fluorinating agent and oxidizer for solid rocket propnts (Ref 6)

**Tetrafluoroammonium Tetrafluoroborate**, NF$_4^+$ BF$_4^-$, mw 176.81, a white solid, decomps betw 240 and 350° into N trifluoride, B trifluoride, and F (Ref 5), Q$_F$ –380 kcal/mole (Ref 5); CA Registry No 15640-93-4

It has been prepd by irradiation of a mixt of B trifluoride, N trifluoride, and F with 3 mev radiation from a Van der Graff generator (O
must be rigorously excluded to avoid explns) (Ref 7); or by irradiation of the same reagents in a sapphire reactor with unfiltered UV radiation (Ref 10). The IR spectrum is given in Refs 5 & 10, and the X-ray diffraction pattern indicates the crystal to be cubic with a 7.35Å (Ref 5). It has been proposed as an oxidizer in solid rocket propellants and as a source of active F radicals for a H fluoride/D fluoride laser (Ref 10).

**Tetrafluoroammonium Hexafluoroantimonate**, NF₄⁺SbF₆⁻, mw 325.76, a white solid, decomps ca 350°C (Ref 1); CA Registry No 16871-76-4

It is prep'd by heating a mixt of N trifluoride, Sb pentfluoride, and F in a Monel tube reactor at 200°C for 2.5 days (Ref 1); or by irradiating the same reagents with UV radiation in a quartz bulb (Ref 9).

Other tetrafluoroammonium salts which have been prep'd are **Tetrafluoroammonium Pentaxo- fluorogermanate**, NF₄⁺GeF₆⁻, decomps 249°C; **Tetrafluoroammonium Hexafluorophosphate**, NF₄⁺PF₆⁻, decomps 245°C; and **Bis(tetrafluoroammonium) Hexafluorogermanate**, (NF₄⁺)₂GeF₆⁻, decomps 238°C (Ref 9).


**Tetrafluorohydrazine** (Dinitrogen Tetrfluoride), N₂F₄, mw 104.01, N 26.9%; a colorl gas at room temp, in the condensed phase it varies from white to blue-black depending on the % N di- fluoride free radical present (see below). This, in turn, depends on how quickly and from what temp the tetrafluorohydrazine is condensed (Ref 4). The odor is described as musty (Ref 7); CA Registry No 12357-40-3

**Physical Properties**: mp –163°C (Ref 7), bp –73°C, crit temp 36°C, crit pres 77 atm (Ref 1); Qₐ 3170cal/mole, Qₐ gas at 25°C = 2.0±2.5kcal/mole (Ref 2).

**Preparation.** Its prep'n was first carried out by the action of metals as F acceptors on N trifluoride in a flow reactor at 375°C, conversion 42–62%, yield 62–71% (Ref 1). It has also been prep'd by the passage of N trifluoride thru a fluidized bed of pow'd C at 400–500°C, conversion 38%, yield 77% (Refs 3 & 3a); or by the oxidn of difluoroamine (Ref 6)

**Explosive Properties.** It undergoes an exp'l reaction with H₂, but concn and temp limits of the expn were not reproducible in Pyrex or stainless steel reactors, probably due to the presence or absence of initiating radicals on the walls. The results became more reproducible after the walls were coated with silicone oil. Addn of tetrafluorohydrazine to H₂/difluoroamine or H₂/N trifluoride mixts caused immediate explns (Ref 9). It also can expld on contact with reducing agents or from high press produced by shock wave or blast (Ref 11).

Its toxicity is high and similar to H fluoride (Ref 11).

**Refrs**: 1) C.B. Colburn & A. Kennedy, JACS 80, 5004 (1958) 2) G.T. Armstrong et al,
"Heat of Formation of Tetrafluorohydrazine", NBS Rept 6684 (Oct 1959), AD-232598

Fluorine Azide (Trinitrogen Fluoride). FN3, mw 61.02, N 73.2%; a greenish yellow gas at room temp, a greenish yellow oily liq (Ref 1); odor similar to C1 dioxide (Ref 1); mp -143⁰ (Ref 3), bp -82⁰ (Ref 1); UV and visible absorption maxima are in Ref 3. It is prepd by fluorination of H azide with F:Ar mixts 1:200 (Ref 2). Best yields are obtained when the ratio of H azide to F is 2:1 (Ref 2). As the danger of exps is great, the reaction must be well shielded (Ref 1). Exps of liq or solid F azide are described as unusually violent and brisk (Ref 1). Evapn of solid or liq F azide frequently results in exps (Ref 2)


Nitrogen Iodides

Iodamide (iodamine). INH2, mw 142.93, N 9.8%; a black solid; prepd by the action of I on liq ammonia at -90⁰ followed by evapn of the excess ammonia; further removal of ammonia under high vacuum converts it to N triiodide (Ref 11). Under apparently similar conditions the same workers later isolated a red complex contg 1 mole of ammonia which loses the mole of ammonia under high vacuum, regenerating the black iodamide (Ref 12)

Nitrogen Triiodide, NI3, mw 394.77, N 3.5%; a black powd, detons when dry, exposed to light, or an elec spark (Refs 8 & 10); Qf 35kcal/mole (Ref 7). It is formed by the interaction of free I or I- on liq, gaseous, or aq ammonia (Refs 1, 8 & 10). N triiodide forms a series of solvates with excess ammonia: NI3.NH3, bright red needles, expids when dry (Ref 2). The damp solid was pumped dry under vacuum at 0⁰, and it detond when the last trace of w was removed; below -11⁰ it decomps slowly (Ref 6); Qf -42 ± 2.0kcal/mole, N-I bond strength 48 ± 4kcal/mole (Ref 14); CA Registry No 14014-86-9

NI3.2NH3, yellow crystals (Ref 5). It was shown later by X-ray diffraction that this is a mixt of a red and a green solvate (Ref 11)

NI3.3NH3, oliv-green needles (Refs 5 & 11); CA Registry No 15823-38-8

NI3.12NH3, a brown-black powd (Ref 4). This was also shown by X-ray diffraction to be a mixt (Ref 11)

Iodine Azide. IN3, mw 168.92, N 24.9%; a black solid, decomps on standing or in the presence of S compds (Refs 9 & 13); CA Registry No 14696-82-3

It is prepd by the action of I on Ag azide (Ref 3); or more easily in sohn by the interaction of I chloride and Na azide (Ref 13). Solns of I azide react readily with olefins to give 2-iodoalkyl azides which lose H iodide to form unsaturated azides (Ref 13)

Nitrogen oxides

Nitrogen Monoxide (Nitrous oxide, Hyponitrous Oxide, Laughing gas). $\text{N}_2\text{O}$, mw 44.02, N 63.65%; colorless gas with sweetish odor and taste, mp $-90.86^\circ$, bp $-88.48^\circ$, d 1.9777 g/l. It is appreciably sol in w and more sol in alc. Commercial prep is by the decomp of AN thru gentle heating; $\text{NH}_2\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. Heating above 200$^\circ$ should be avoided because the salt will start to decomp with formation of NO, $\text{N}_2$, and $\text{NH}_3$. If the salt is heated to slightly above 250$^\circ$, an expln occurs. Nitrogen monoxide supports combustion more vigorously than air, since, on decomp, it yields a gas contg 1/3 its vol of $\text{O}_2$ as compared with 1/5 with air.

Although it forms expl mixts with CO, $\text{NH}_3$, $\text{CS}_2$, and phosphine, it is not used in the expls industry. It also forms combustible mixts with NO and fuels such as butane, benz, cyclohexane and $\text{p}$-xylene (Ref 8).

Nitrogen monoxide is used as an oxidizer in bipropellant systems with carbon monoxide or methanol-w as fuels, and it is added to $\text{N}_2\text{O}_4$ to advantageously modify the frp and bp of this oxidizer. It is also employed as a high enthalpy flow medium in hypersonic wind tunnels (Ref 10), and as an oxidizing gas in atomic absorption spectroscopy (Ref 12). $Q_f$ $= 19.7$ kcal/mole (Ref 3).


Nitrogen Oxide (Nitric oxide). NO, mw 30.01, N 46.68%; colorless gas, blue in liq or solid form; mp $-163.6^\circ$, bp $-151.8^\circ$, d 1.3402g/l, 1.269 g/l at $-150.2^\circ$ (liq), RI 1.330 at $-90^\circ$. Sol in w, 7.34ml at 0$^\circ$; alc, 26.6ml; sulfuric acid, 3.5ml, aq Fe sulfate and conc nitric acid

Nearly pure NO can be prepd by heating a mixt of K nitrate, Fe sulfate and dil sulfuric acid; $6\text{FeSO}_4+2\text{HNO}_3+\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3+2\text{NO}+4\text{H}_2\text{O}$. It is also produced by the action of UV light or lightning on the atm, and as a by-product of nuclear and chemical explns (Ref 1).

Nitric oxide is the most stable oxide of nitrogen. It decomp above 1000$^\circ$ and will not support combustion below this temp. When mixed with hydrogen, it can be expld by a long duration, intense electric spark (Ref 8). It is very endothermic, its $Q_f$ being $-21,575$cal/g at RT (Ref 5).

The gas has no practical application as an expl. It is of importance, however, as an additive to $\text{N}_2\text{O}_4$ to depress the frp of this bi-propellant hypergolic oxidizer (Ref 7). It is also
one of the principal compds dealt with in the manuf of nitric acid by the ammonia oxidn process, as well as in the manuf of expls by various nitration procedures (Refs 9 & 10)

The inhalation of concns of 200 to 700 ppm may be fatal after even very short exposure (Ref 11). Also see under Nitrous Furnes in this Vol

Refs: 1) Gmelin, Syst 4 (1955), 600–736  
2) Scott & Furman (1939), 2346 & 2400  
5) Thorpe B (1947), 517–22  
6) Mollor B (1947), 417–49  
8) Partington (1950), 570–73 & 575  
9) Urbańska J (1964), 77  
11) Sax (1975), 961–R  
12) ChemRubHdbk (1975), B-115

Nitrogen Pentoxide (Dinitrogen pentoxide, Nitric anhydride), N₂O₅, mw 108.02, N 25.94%; white crys, very hygr; mp 29.5°C; pure N₂O₅ sublimes at 32.4°C; bp, starts to boil at about 45°C having previously darkened in color due to partial decomp; d 2.05g/cc at 15/4°C, 1.642 g/cc at 18°C. Sol in w and nitric acid to about 30 wt% at 25°C. See Ref 9 for properties of N₂O₅ solns in nitric acid

Prepd by dehydrating concd nitric acid with phosphorus pentoxide (Refs 3 & 4). Expls if heated suddenly (Ref 4). Can also be prepd by the flash photolysis of O₂–N₂O–He mixts (Ref 11), and by the radiolysis of N₂O₄–HNO₃ with γ rays (Ref 12).

Its principal military use is as a nitrating agent, either in the vapor phase or when dissolved in an inert solvent such as CCl₄, for such substances as alkyl nitriles, cellulose and Nitrobenzene (Refs 2a, 8 & 13)

Refs: 1) Gmelin, Syst 4 (1955), 818–37  
2) Scott & Furman (1939), 2400  
2a) H. Aaronson, "Evaluate Method of Nitrating Cellulose Developed by the Stein Hall Co", PATR 1331 (1943)  
4) Partington (1950), 569  
5) F. Miles, "Nitric Acid Manufacture and Uses", Oxford Univ Press, London (1961), 20  
6) W. Jolly, "The Inorganic Chemistry of Nitrogen", W.A. Benjamin, Inc, NY (1964), 70 & 83  
7) Hackh's (1972), 457  
8) Urbanski J (1964), 10, 11, 19, 61, 105, 106 & 107  
13) G.B. Gustave & N.W. Cannon, USP 3549686 & CA 74, 99452 (1971)

Nitrogen Tetroxide (Nitrogen Peroxide, Nitrogen Dioxide, Dinitrogen Tetroxide), NO₂ or N₂O₄, mw 46.01 or 92.02, N 30.45%, mp −9.9°C, bp 21.20°C, d 1.4494 g/cc at 20/20°C; RI 1.40 at 20°C. Reddish-brown gas at RT with a pungent smell, having the formula N₂O₄. When heated it becomes paler, because of dissociation; N₂O₄ = 2NO₂; and finally colorl, because of decomp to NO and O. When cooled it becomes a dark orange-red liq which becomes paler on further cooling, and finally becomes a nearly colorl solid, N₂O₄. 

Sol in w, alk, carbon disulfide, chl, nitric and sulfuric acids

Prepd industrially from nitric acid and air. A convenient lab prepn is by decomp of Pb nitrate by heat; 2Pb(NO₃)₄ = 2PbO + 4NO₂ + O₂ (Refs 2, 3, 4, 10 & 11).

Nitrogen tetroxide is formed as an undesirable product in several instances, eg, during the storage of some energetic materials, particularly NC, NG and mixts contg them, such as proplnts and Dynamite. In these the nitric esters decomp at elevated temps. In some cases, even such stable nitrocmpds as TNT can begin to evolve NO₂ when stored at higher than ambient temps.
This usually occurs when all the acid was not neutralized in the washing process, and remains in the finished product to react with the nitrocompd in storage.

Nitrogen tetroxide is also formed during the manuf of nitric acid and in the nitration of org substances.

Perhaps its most undesirable reaction is that with ozone; \( \text{N}_2\text{O}_4 + \text{O}_3 = \text{N}_2\text{O}_5 + \text{O}_2 \). Under closed vessel conditions, using an electric spark, this reaction is explosive (Ref 33). However, when the reaction occurs in the atm, it proceeds at a slower rate, and effectively works to strip the UV shield of ozone surrounding the earth greatly increasing the possibility of skin cancer (Ref 40).

When liq ammonia is mixed with solid \( \text{N}_2\text{O}_4 \) at about \(-80^\circ\text{C}\), an expl occurs. The action of gaseous ammonia at \(-20^\circ\text{C}\) is less vigorous (Ref 11). Spontaneous exps occur on contact between liq \( \text{N}_2\text{O}_4 \) and hydrazine-type fuels (Ref 18). Contact-type exps also occur with such materials as acetic anhydride, liq ammonia, methyl and ethyl nitrate, and propylene (Ref 33). \( \text{N}_2\text{O}_4 \) also forms expls with incompletely halogenated hydrocarbons, NGu, carbon disulfide, etc (Ref 33). The effect of spontaneous decmpn by oxidation-reduction reactions when \( \text{N}_2\text{O}_4 \) is mixed with a number of fuels (hydrazine, gasoline, liq paraffin, etc) has resulted in its extensive use in liq propellant engines (Refs 12, 22, 27 & 35).

Nitrogen tetroxide is a powerful oxidizing agent, as well as a good nitrating agent (Refs 18 & 24). Hence, extreme care must be taken in handling and storage (Refs 25, 28 & 33).

A recommended USAF guide in this connection is Ref 20. Compatibility studies with spacecraft materials are reported in Refs 23, 29 & 32.

Pure \( \text{N}_2\text{O}_4 \) forms nitrocompds readily at elevated temps with either aliphatic or aromatic hydrocarbons in the gaseous or vapor state. It therefore finds extensive use in the commercial prep of nitrocompds in both the exps and dye industries (Ref 24). Nitrations can be conducted in either the liq or vapor phase (Ref 8), and the \( \text{N}_2\text{O}_4 \) can be used as such or dissolved in an inert solvent such as \( \text{CCl}_4 \). Recently, Castorina et al (Refs 19 & 36) have shown that gamma irradiated liq \( \text{N}_2\text{O}_4 \) can be ionized to the extent of being able to directly nitrate benz to NB and DNB at RT.

Because of its powerful oxidizing properties, nitrogen tetroxide has also been used in mixts with combustible materials in the so-called Sprangel type expls. The first expls of this type were Pantastic, proposed by Turpin in 1881. In them liq \( \text{N}_2\text{O}_4 \) was mixed just before use with a combustible substance such as CS\(_2\), NB or light petroleum. These mixts were extremely sensitive to shock, and had to be handled with the greatest of care. Another expl mixt contg \( \text{N}_2\text{O}_4 \) was Anilite (see Vol 1, A443-R), used by the French during WWI as a bomb filler. PicArsn evaluated Myrite (see in this Vol), a mixt of NO\(_2\) and CS\(_2\), and concluded that it was not suitable for military use.

Nitrogen tetroxide expls were thoroughly investigated by Kast and Günther (Ref 4), who tested mixts of liq \( \text{N}_2\text{O}_4 \) with the following substances: \( \text{C}_6\text{H}_6 \), TNT, \( \text{C}_7\text{H}_8 \), NB, \( \text{CCl}_4 \) and CS\(_2\). They found that only mixts with NB and CS\(_2\) were strongly expl, and that both were fairly stable on storage at RT, although NB is slowly attacked by \( \text{N}_2\text{O}_4 \). Both mixts were easily absorbed by kieselguhr, resulting in soft, non-plastic masses which exhibited fp's too high for military use. In order to counteract this, Kast and Günther proposed using 35 parts of a 65/35 mixt of NB and CS\(_2\), to which was added 65 parts of \( \text{N}_2\text{O}_4 \). The expl properties of this mixt were:

**Brissance.** By Kast app ("Stauchprobe") using a 10.5mm high Cu cylinder; 4.5mm compression vs 5.1mm for NG and 4.0mm for PA. **Impact Sensitivity.** As detd in a special app designed for liq expls; less sensitive than NG and more sensitive than PA.

**Trautz Pb Block Expansion.** 435cc with 10g sample vs 493cc for NG and 305cc for PA.

More recent work in liq expls using \( \text{N}_2\text{O}_4 \) is that of Herickes and Ribovich (Ref 14) who made a two year study for the purpose of providing a material which could be used for mine field clearance. It resulted in two stoichimetric mixts, one of \( \text{N}_2\text{O}_4 \)-benz (18.5 wt % benz), and the other of \( \text{N}_2\text{O}_4 \)-nitromethane (64 wt % NM). These mixts exhibited the fol-
lowsing properties:

**Detonation Rate.** For both mixes at 0°, 6900m/sec

**Burr Mines Card Gap Test.** For both mixes, over 2000 mils

**Power by Plate Dent Test.** For both mixes, using a 4” thick steel plate, 0.133” indentation

**Rifle Bullet Impact.** Detonation in 5/5 trials with either mix

The conclusion drawn from these and other tests was that since these liq N₂O₄ expls were relatively short lived when exposed to air, reacted with w, were toxic, and propagated unsatisfactorily on the ground, that they were not practical for mine clearing use

Nitrogen tetroxide is one of the most insidious gases in terms of human toxicity. Inflammation of the lungs may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. 100ppm is dangerous for even a short exposure, and 200 ppm may be fatal (Ref 25). Also see under Nitrous Fumes in this Vol

There is no US military specification for Nitrogen tetroxide

For additional information on Nitrogen tetroxide, see under Liquid Propellants in Vol 7, L34-R to L44-R; Hypersonic Propellants in Vol 7, H254-L to H259-R; Nitrogen Determination in Energetic Materials, and Mass Spectrometry in this Vol

Refs: 1) Gmelin, Syst 4 (1955), 748–818

Nitrogen Peroxide. Same as Nitrogen Dioxide; see under Nitrogen Oxides in this Vol

Nitrogen Selenide. (Selenium Nitride). See under List of Nitride Compounds in this Vol

Nitrogen Sulfide. (Sulfur Nitride, Nitrogen Tetrasulfide). See under List of Nitride Compounds in this Vol

Nitrogen Trioxylfluoride (Fluorine Nitrate, Perinyl Fluoride). NO$_3$F, mw 81.01, N 17.29%, F 23.45%; colorless, irritating gas; bp about −42°. SI sol in w, from which it liberates oxygen

First prep and described in 1934 by Cady (Ref 4) by passing fluorine, dill with N, O or air, thru a specially constructed app made of Ni, Pt and Monel metal contg approx 3N nitric acid cooled to 0° or below. The resulting gaseous product was collected and analyzed. Later, Ruff et al (Ref 5) showed that the use of 100% nitric acid in a quartz app at room temp was more advantageous. Prior to the above work, Moissan in 1891 (Ref 3) observed that expls occurred when fluorine was passed thru concd nitric acid. Yost et al (Ref 6) obtained NO$_3$F from a fluorine reaction with solid K nitrate, and its prep and general props were confirmed by Hill et al (Ref 8)

NO$_3$F is a powerful oxidizing agent, liberating iodine from iodides; NO$_3$F+2KI = KNO$_3$+I$_2$+KF. The gas is stable at room temp, but expls violently on heating


Nitro-α-Glucoheptose. See d-α-Glucoheptose

Hexanitrate in Vol 6, G82-L

Nitroglucosan. See β-Glucosan-2,3,4-trinitrate in Vol 6, G83-R

Nitroglucose. See d-Glucose Pentanitrate in Vol 6, G83-R

Nitroglucosides. Wrightsman patented the prep of expls by the nitration of a methanol soln of glucosides, or a polyhydric alc soln of polysaccharides

Ref: A. Wrightsman, USP 1836568 (1931) & CA 26, 1125 (1932)

Nitroglycerin (Nitroglycerol). See Glycerol

Trinitrate or Nitroglycerin (NG) in Vol 6, G98-R, and in Vol 5, D1593-L to D1594-L
Nitroglycerin-Nitrocellulose Dynamites (Ger). Several Dynamites suitable for rock blasting or for use in potash mines were prep'd by processing surplus WWI double-base propn-lts and mixing the pulverized products with other ingredients such as organic nitrocompsds, inorganic nitrates, etc. Among these were Energet or Mining List No 33 Nitroglycerin Powder: According to Naoum (Ref 1, p 449), the Nobel Co ground different types of double-base proplnt in Excelsior Mills between steel discs, with an abundant flow of w, to a particle size of 0.5 to 2mm, dried the material, incorporated a variety of ingredients, and packed it in cartridges 25 to 30mm in diameter. The compn formulation was NG 30 to 40 and NC 70 to 60%, with added nitroderivatives of toluene and/or naphthalene 0 to 5, and paraffin and/or urethane and/or carbamide and/or dicyandiamide 0 to 10%. Its expl properties were: strength by Trauzl Test, 330 to 350cc, and detonation velocity 3000 to 5000m/sec. The mining authorities prescribed the use of strongest blasting cap to ensure detonation, but when well confined, a fuse alone caused expln (See also Ref 3, E1; Ref 4, Ger 42-L & Ger 121-L).

Lehalleur (Ref 2) states that Energet can be prep'd by wetting small grains of double-base proplnt in a kneader with equal quantities of such volatile solvents as acet and furfuro, adding liq aromatic nitrocompsds and other ingredients, and then kneading the mixt until it is thoroughly blended. Finally, the solvents were removed by evapn (See also Ref 4, Ger 42-L).

Triwestfaltl SN had the same compn as Energet but was prep'd by WASAG (Westfälisch-anhaltische Sprengstoff Aktiengesellschaft) by crushing the proplnt in rollers or edge runners to thin plates and then reducing it to small grains (Refs 1 & 4).

Other expls prep'd from surplus propn-lts included Mining List No 35 Explosive: NG with NC jelly 94 to 96, and 6 to 4 parts of a 50% aq soln of Ca nitrate (Refs 1 & 4); Mining List No 36 Explosive: NG with NC jelly 97 to 99, and 3 to 1 parts of substituted urethanes (Refs 1 & 4).

Refs: 1) Naoum, NG (1928), 449–50 2) Pepin Lehalleur (1935), 457 3) Clift & Fedoroff 2 (1943), E1 (Energet) 4) PATR 2510 (1958), Ger 42 (Energet), Ger 121 (NG-NC expls), and Ger 209 (Triwestfaltl SN).

Nitroglycerin Powder. Same as Energet (see above).

Nitroglycerin Shells. See Vol 6, G108-L.

Nitroglycols or Glycol Nitrates. See Vol 5, D1594-L & Vol 6, G114-R to G115-L.

Nitroglyoxime. See Vol 6, G119-L.

Nitroguanidine. See Vol 6, G154-Rff.


Nitrohydantoin. See Vol 7, H188-L.

Nitrohydroene. Nitrated mixt of glycerol and sugar introduced by DuPont in 1911 as a component of low-freezing Dynamites. Such expls found extensive use in the USA until nitrated glycol was introduced in 1926. Ref: Anon, IEC 50: 41A (1958).

Nitroindene Polymer (N.I.P.). Evaluated at PicArsn as a substitute for charcoal in fuze powders. The N.I.P. fuze powders gave longer burning times and lower dispersions in M54 Time Fuzes under rotation and reduced pressure than the corresponding charcoal powders. They were also more sensitive to impact. Ref: D. Hart, “Investigation of the Use of Nitroindene Polymer in Powder for M54 Time Fuze”, PATR 1296 (1943) & PATR 1826 (1945).

Nitro-iso-butane triol (Trimethylol nitromethane). See Vol 2, B371-R.
Nitrokrakites. Expls invented by Alvisi in 1899 which contained AN as the principle ingredient, together with NG and NC
Ref: Daniel (1902), 396–7 & 558

Nitrol. Early Brit plastic safety expl, patented by O. Silberrad in 1912 (Ref 2). A typical formulation is Nitrol 10, highly nitrated benzene hydrocarbons 20, collodion cotton 0.5, and AN 69.5%. Under the same name, O. Silberrad took Brit and US patents on expl mixes contg Nitromethylnaphthalene 20–25, oxidizer (nitrates, chlorates, perchlorates, etc) 50–60, collodion cotton 0–5 and woodmeal 0–5% (Ref 1)
Refs: 1) O. Silberrad, BritP 19381 (1912) & USP 1092758 (1914) 2) Colver (1938), 261

Nitrolactose. See Vol 7, L1-R to L2-R

Nitrolic Acids. Acids of the general formula R.C(NO2).NO2 or R.C(NO OH).NO where R stands for CH3, C2H5, etc. Nitrolic acids can be prepd by mixing, in the absence of O2, a primary nitroparaffin withaq alkali (about 1:1), an inorganic nitrite such as NaNO2, and then gradually adding the mixt to a mineral acid at below 15°. The following reaction takes place: RCH2.NO2+HO.NO -> R.C(NO2).NO2+H2O. The resulting compds are yellowish oils, which turn red in the presence of alkalis. These red salts are usually very powerful expls. Some Nitrolic acids, on being added to Diesel oils, make the ignition more effective

Ethynitrolic Acid (Nitroacetoxime, Acetnitril-sulfer in Ger). H2C.C(NO2).NO2, mw 104.07, N 26.92%, OB to CO2 -46.1%, colorl to yel rhombic crystals, mp 84–85° (decomp), bp decmmps with expl violence. Sol in w, alc, eth and in most common org solvents. Can be prepd by one of the following methods: 1) by dissolving nitroethane inaq KOH, adding Na nitrite, and acidifying with dil sulfuric acid; 2) by treating isonitrosopropionic acid with N2O4; and 3) by acidifying a soln of Na 2-nitropropanate and Na nitrite in dil KOH with 5N sulfuric acid at -10°

Ethynitrolic acid is an expl compd and forms numerous metallic salts, some of which are expls:
Potassium Salt. KC2H3O2N2, colorl amorph powder, sl sol in methanol; a weak expl
Silver Salt. AgC2H3O2N2, white amorph powder, insol in w and dil alc. Sensitive to light, expls on heating

Methylnitrolic Acid (Nitroformoxime, Nitromethanoxim in Ger). HC(N=NO)NO2, mw 90.04, N 31.11%, OB to CO2 0.0%, colorl needles, mp 64–68° (decomp), bp expls below 100°, v sol in w, alc and eth. Can be prepd by the action of a mixt of K nitrite and sulfuric acid on nitromethane

Propynitrolic Acid. H3C.CH2.C(N=NO)NO2, mw 118.09, N 23.72%, OB to CO2 -81.3%, prisms from alc, mp 66°, bp deflagrates on rapid heating, sol in w, alc and eth. Can be prepd by treating potassium 1-nitropropanate with K nitrite and dil sulfuric acid. Nygaard prepd it (Refs 2 & 3) by dissolving 0.2 mol (105p by wt) of 1-nitropropane in 0.22 mol Na hydroxide (10% soln), and adding 16.8p of Na nitrate with stirring. After adding 100p of ice and cooling the mixt in an ice-salt bath, a soln of 50.6p of concd HCl and 110p of w were added, while the temp was maintained between -12° and +2°. It was then allowed to stand for 16 hrs. Extn with eth produced propynitrolic acid. It is a weak expl

Nitrolin. Fr name for nitrated flax
Nitroline. An expl prepd by the nitration of stearin (12p) and sugar syrup (15p) with nitric (80p) and sulfuric (170p) acids. It was used in compound expts called Vigorine or Vigorite, patented in Engl in 1875:
No 1: Nitroline 40, Cellulosa 22, K nitrate 22
and K chloride 16%
No 2: Nitroline 30, Cellulosa 10, K nitrate 20,
K chloride 20, sawdust 10 and peafloir 10%.
Cellulosa is prepd by nitrating 3p of peafloir
with a mixed acid contg nitric (5p) and sulfuric
(10p) acids. These expts were sometimes called
American Vigorines
Ref: Daniel (1902), 72-3 & 785

Nitrolit. See 2,4,6-Trinitroanisole in Vol 1,
A450-L to A452-R

Nitrolite. An expl patented by Carl Lamm contg
NG 94–99p; K, Na or Amm nitrate 50–150p;
NC, nitrostarch or nitrostraw 1–6p; with or
without NB
Ref: Daniel (1902), 560

Nitrokrut. An expl patented in 1876 by Berg
of Sweden contg NG 5–40, K & Na nitrates
25–75, and K chloride 5–50%
Ref: Daniel (1902), 560

Nitromagnite (Dynamagnite). Dynamite invented
in 1878 by E. Jones consisting of 20% NG ab-
sorbed in magnesium alba, which is a mix of
Mg hydrocarbomates. It is similar in cmpn to the
Fulgurites (see Vol 6, F215-L), manufd in
Hungary and by the Hercules Powder Co at
one time in the USA
Ref: Daniel (1902), 560

Nitromaltose. See in this Vol under Maltose
Octanitrate, M10-R

Nitromannitane. See in this Vol under Manni-
tane Tetranitrate, M13-L

Nitromannite (Nitromannitol). See in this Vol
under Mannitol and Derivatives, M13-Lff

Nitromannose. See under D-Mannose Pentanitrate in this Vol, M17-L

Nitrometer. An app used for the estimation of
nitrogen in inorganic and organic nitrates by
their reaction with Hg and sulfuric acid. For
details of construction and operation see Vol 1,
A373-L to A377-L

It was invented by Lunge in 1890 under the
name “gasvolumeter” (Ref 1). Ten years later,
in the USA, it was modified and improved by
F.I. duPont and described by Pitman as the
duPont Nitrometer” (Ref 2). At present, both
macro and semi-micro nitrometers are in use, the
latter being designed by Elving and McElroy
(Ref 7)
Refs: 1) G. Lunge, ZAngChem 3, 139–44
(1890); Ibid, JSCI 9, 547–9 (1890); Ibid, JSCI
20, 100–2 (1901) 2) J.R. Pitman, JSCI 19,
982–86 (1900) 3) W.C. Cope & J. Barab,
JACS 38, 2552–8 (1916) 4) M. Marquetry
& D. Florentin, BullFr 9, 231–40 (1911); Ibid,
MP 21, 326 (1924) 5) J. Witt, SS 15, 145
(1920) 6) H.W. Webb & M. Taylor, JSCI
41, 362T (1922) 7) P.J. Elving & W.R.
McElroy, IEC (AnalEd) 14, 84 (1942) 8) M.
Roth et al, “Nitrometer Reaction Bulb” PATR
2579 (1958)

Nitromethane (Nitrocarbol). See under Methane
in this Vol, M69-L ff

Nitromethoxymethoxymethyl Nitrate (Nitro-
nitroxymethyl). O₃N.CH₂.O.CH₂.O.CH₂.O.NO₂,
mw 182.1, N 15.38%, OB to CO₂ –17.6%, oily
liq, bp 88–89° at 9mm. Usually present in the
products of nitration of symm-dichloromethyl
ether in the prep of nitromethoxymethyl
nitrate (see below), from which it can be sepd
by fractional distn in vac at about 90°. It is a
powerful expl. Houben and Pfankuch (Ref 2)
reported that when they attempted
the vac distn at 110°, violent expln occurred
Refs: 1) Bell 1, [649] 2) J. Houbsn & E.
Pfankuch, Ber 59, 87 & 89 (1926)
Nitromethoxymethyl Nitrate.

O₂N,CH₂.O,CH₂.O,NO₂, mw 152.07, N 18.42%, OB to CO₂ 50%; colorless, volatile oil; d 1.52206 g/cc at 4°, 1.5005 g/cc at 12°; RI 1.4328 at 12°.

Can be prep'd by treating symm-dichloromethyl ether with mixed nitric-sulfuric acids; C₂H₅OCH₂Cl₂O₃N₂O₃ (nitrogen pentoxide) = O₂NCH₂OCH₂ONO₂ + Cl₂. It is a very powerful expl, extremely shock sensitive. It is an excellent solvent for NC, even at temps as low as 0°. It has been claimed that a gel cong 7% NC (12.11% N) with this compd developed a greater gas volume on expl than a corresponding mixt with NC.


Nitromethyl-iso-nitramine. CH(N₂O₂H)(NO₂H), mw 121.06, N 34.71%, OB to CO₂ +6.61%. It forms expl heavy metal salts, which according to Urbanski, are weaker initiators than the corresponding metal salts of methylendi-isonitramine. The increasing order of brisance of these salts, when primed with MF, in the Pb plate test were Na, Ca, Ba, Ti and Pb.


N'-Nitro-N-methyleneaminoguanidine.

(O₂N)₂NH.C(NH₃).NH₂.CH₂, mw 131.10, N 53.42%, OB to CO₂ -54.9%, needles, sl sol in w. Can be prep'd from N'-nitro-N-methyleneaminoguanidine and formaldehyde in w. Explds on heating.

Ref: Bell 3, [101]

Nitronaphthalenes. See under Naphthalene and Derivatives in this Vol

Nitronaphthols. See under Naphthol and Derivatives in this Vol

Nitro-α-methyl-d-mannosite. See α-Methylmannite Tetranitrate in this Vol

Nitron (4,5-Dihydro-1,4-diphenyl-3,5-phenyliminine-1,2,4-triazole, or 1,4-Diphenyl-3,5-endoanilino-4,5-dihydro-1,2,4-triazole).

N⁺(C₆H₅)₂.CH₂.N⁺, C₂₀H₁₆N₁₄, mw 312.36; intensely yel leaflets from alc, solvated needles from chlf; mp 189–90° decompn. Practically insol in w; sol in alc, benz, acet, chlf, et acet and dill acids; sl sol in eth.

Nitron was prep'd in 1905 by M. Bush by heating N'-anilino-N,N'-diphenylguanidine with 90% formic acid in a press tube at 175° (Ref 2). Other methods are given in Ref 1.

Nitron forms v sl compds with metallic nitrates, perchlorates, picrates, trinitroresylates, as well as with organic nitrates such as NG, NC, Nitroanisole, etc, and can serve as a gravimetric reagent. The Nitron method for the detn of N is based on the fact that it ppts inorganic nitrates from w soln, and forms an insol addition product, C₂₀H₁₆N₁₄.HNO₃, mw 375.3.

Refs: 1) Bell 26, 349 2) M. Busch, Ber 38, 858 & 4054 (1905) & JCS (Abst) 86, I, 307 (1905) 3) Ibid, Ber 38, 861–66 (1905) [Quant detn of nitric acid by the Nitron method]

4) M. Busch & S. Schneider, SS 1, 232–33 (1906) [Detn of N in NC by the Nitron method and comparison of results with those obtained by nitrometer]


7) Merck (1968), 740-L

8) CondChemDict (1971), 624-L

9) Hackh’s (1972), 460-L

2-Nitro-2-(m-nitrophenyl)-propanediol-1,3 Dinitrato (2-Nitro-2-(3'-nitrophenyl)-propanediol-1,3-diol Dinitrato).

(O₂N)₂.C₆H₄.C(NO₂)₂(CH₂.O.NO₂)₂, mw 332.19, N 16.86%, OB to CO₂ -57.8%, colorl crysts from alc, mp 72.6–73.6°, bp ignites at 270° but does not expld even when heated at 360°. Insol in w and moderately sol in alc.
Was prep'd by Fieser and Gates (Ref) by adding 200 mgs of 2-nitro-2-(m-nitrophenyl)-propanediol-1,3 to a well-cooled mixt of 0.4ml of concd sulfuric and 0.15ml of nitric (d 1.41 g/cc) acids, previously freed from nitrous acid by the addition of urea. After soln was complete, the liq was left standing for 10 minutes and was then drowned in ice w. The heavy oil which separated was treated with alc and left standing until crystn took place (after two weeks). A second recrystn from alc gave a fairly pure product.

It is an expl which is slightly more powerful than TNT (114% as detd by ballistic mortar at the Res Lab of NDRAC at Bruceton, Pa), and slightly less sensitive to impact. Its thermal stability is satisfactory and it is nonhygroscopic.

Ref: L.F. Fieser & M. Gates, JACS 68, 2249 (1946) & CA 41, 733 (1947)

Nitropenterythritite. Fr for Pentaerythritol Tetranitrate

1-(o-Nitrophenyl)-2-nitroethyl Nitrate (α-(2-Nitrophenyl)-β-nitroethyl Nitrate),
O₂N.C₆H₄.CH(O.NO₂).CH₂.NO₂₂, mw 257.16, N 16.34%, OB to CO₂ 77.8%; colorl, diamond shaped crystls; mp 132.2–132.7°; bp, does not decom when heated to 360°. Sol in acet, v sol in alc.

Can be prep'd by condensing o-nitrobenzaldehyde and nitromethane, with triethylamine as solvent, and then adding concd nitric acid with cooling; O₂N.C₆H₄.CH.OH.CH₃NO₂.HNO₃ → O₂N.C₆H₄.CH(NO₂)₂.CH₃NO₂.H₂O. It is decompd by hot w with the formation of nitrous acid.

It is an expl which is as powerful as TNT (99% by ballistic mortar), but more sensitive to impact, being comparable to Tetryl. Its 120° Vacuum Stability Test yields 8cc for a 5g sample in 8 hours, as compared with 6.5cc/5g sample in 15 hours for PETN and 3.8cc/5g sample in 48 hours for Tetryl.

Ref: 1) Bell, not listed in General Index 2) L.F. Fieser & W.H. Daudt, JACS 68, 2248–9 (1946)

Nitrophycite. An older name for Erythritol Tetranitrate

Ref: Daniel (1902), 480

Nitropolene (Nitropolene). A mining expl invented by Volkmann contg K nitrate, K ferrocyanide and sawdust.

Ref: Daniel (1902), 568 & 788

Nitropolyglycerin. Same as Tetranitroglycerin; see in Vol 5, D1261-L

NITROPOLYMERS

The term “nitropolymer” refers to nitrated polymeric comps, usually thermoplastic, having nitro-carbon bonding, viz:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\cdot \text{C} & \cdot \text{C} \\
\text{NO₂} & \text{H}
\end{align*}
\]

There are quite a few expl comps in this category, including polymerized nitro oleins. Since nitro oleins are of especial interest they are presented in a separate article in this Vol.

The nitro ion adds to a double bond in a manner similar to the action of halogens. It can be generated by either nitric acid, N₂O₅ or N₂O₄. In some instances the polymer is nitrated after polymerization with many of the polynitrethanes; usually, however, a nitrated monomer is reacted with itself (called homopolymerization) or with a different monomer species (called heteropolymerization). Some monomers are self polymerizing when exposed to air, forming viscous, gummy polymers. Some require catalysts and form crystalline (cross-linked) polymers. However, postpolymerization nitratation usually eliminates cross-linking and results in an amorphous polymer with no well defined mp.

The selected nitropolymers in this article are presented alphabetically with respect to their polymeric designation, viz, (poly) acrylate, (poly) amide, (poly) ester, etc. Each of these polymeric types is defined in each entry by graphic formula. The sole amide and polyester discussed
as well as the ureas and urethanones were developed by the Aerojet General Corp of Azusa, Calif, under ONR contracts during the 1940's and 1950's. These compds were referred to in Vol 1, A108-L under "Aerojet Propellants". They were not listed at the time of publication of Vol 1 because of their confidential classification. However, they are now unclassified and, therefore, can be treated


Nitroallyl Acetate Polymer.

Monomer

Nitroallyl Acetate. H₂C:CH₂(C=O)C₂H₃,

\[ \text{NO}_2 \]

mw 145.13, N 9.66%, OB to CO₂ 104.73%, It green mobile liq, mp 17.5⁰, 68° at 2mm, d 1.217g/cc, RI 1.4528 at 25⁰. V sol in acet, toluene and alc; sol in w. Prepn of the compd is in three steps: 1) gas phase reaction of methyl nitrate with formaldehyde to yield dimethyl nitromethane;

\[ \text{CH}_3\text{NO}_2(\text{g})+\text{CH}_2\text{O}(\text{g}) \rightarrow (\text{CH}_2\text{OH})_2\text{CHNO}_2(\text{g}), \]

2) esterification using acetic acid in the liq phase;

\[ (\text{CH}_2\text{OH})_2\text{CHNO}_2(\text{liq})+\text{CH}_3\text{COOH}(\text{liq}) \rightarrow (\text{CH}_2\text{OOCCH}_3)_2\text{CHNO}_2(\text{liq}) \]

3) selective oxidation to a mono ester olefin using mild conditions such as dil aq KMnO₄.

\[ \begin{align*}
\text{CH}_2\text{OOCCH}_3 & \quad \text{MILD} \quad \text{CH}_2 \\
\text{CH}_2\text{OCH}_3 & \quad \text{OXID} \quad \text{CNO}_2 \\
\text{CH}_2\text{OOCCH}_3 & \quad \text{CH}_2\text{OOCCH}_3
\end{align*} \]

Polymer

Nitroallyl Acetate Polymer.

\[ \begin{align*}
\text{CH}_2 & \\
\text{CNO}_2 & \\
\text{CH}_2\text{OOCCH}_3
\end{align*} \]

mw (145.13)ₙ. Prepn of polymer by exposure of the monomer to air at RT

The polymer is compatible with both NC and rubber at all ratios of from 20–80% (compd/material). Impact sensitivity using BM machine with a 2kg weight is no functioning at 100cm (RDX is 30cm). Q₉ 4.240cal/g at 25⁰(Ref liq H₂O). Qₙ⁰ 94cal at 25⁰. Thermal stability at 65-5⁰ using a 1–3g sample and KI-starch paper showed color in 19min, no appearance change in 5hrs (Ref NC, no color in 10min); during the 134.5⁰ thermal stability test in which methyl violet paper is used, expl decomp occurred in 10min (Ref NC, 30min, no color)

Considered an irritant, fumes dangerous to inhale; an expl hazard especially with heat or oxidant exposure


Nitro Ethyl Acrylate Polymers. See Vol 6, E201-R to E202-R

2,2-Dinitropropylacrylate (DNPA).

Monomer

\[ \begin{align*}
\text{H} & \quad \text{O} \quad \text{H} \quad \text{NO}_2 \quad \\
\text{C} & \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{—CH} \\
\text{H} & \quad \text{H} \quad \text{H} \quad \text{NO}_2 \quad \text{H}
\end{align*} \]

mw 204.10, N 13.73%, OB to CO₂ 109.75%, off-wh cryst, mp 175⁰ (decomp), bp 96° at 0.2mm, d 1.302g/cc at 60/25⁰, RI 1.4596. Sol in acet and dimethylthionate. DNPA is prepd by dissolving 2,2-dinitropropanol and acrylic chloride in CCl₄ and heating for 12 hrs at 55⁰. The dried product of the reaction is then mixed with powd Ag and vac disint. A 55% yield is obt. Q₉ 1.06kcal/g; Qₙ 539cal/g; heat test at 120⁰ on a 0.25g sample exposed for 22 hrs yielded 0.04–0.06cc of gas. Impact sensitivity on sandpaper using a 5kg wt is over 177cm for 50% all-fire probability

Rapid absorption of DNPA causes marked irritation of respiratory tract, skin and eyes

DNPA is used as a binder in artillery propellents and in concns of 10–15% has a burning
rate of 0.19—0.62 inch/sec at 1000 psi (Ref 3). DNPA monomer has also been copolymerized with methyl acrylate and hydroxy alkyl acrylates to form a terpolymer useful as an expl binder (Ref 8) polymer (p-DNPA).

\[ [-\text{CH}_2\text{-CH.CO.}\text{CH}_2\text{-C(NO}_2\text{)}_2\text{-CH}_3\text{]}_n, \text{ mw} \ (204.10)_n, \text{ mp} 248^\circ \text{ (decomp)}, \text{ d} 1.379 g/cc. \text{ Sol in dimethyl thionate. The polymer is prep} \text{ by reacting a mix of DNPA, toluene and azobisisobutyronitrile under dry N}_2 \text{ at 80}^\circ \text{ for 45 mins. A 25\% conversion is obt} \text{d}.

Poly-DNPA has an expln temp at cons vol of 250\%, deton vel at RT is 6100m/sec. Tests. P-DNPA can be dets spectrophotometrically using a calibr curve from the absorption of the carbonyl group near 1750cm\(^{-1}\) while dissolved in dimethyl thionate.


Of the many nitro polymers developed as propiots by Aeroljet General Corp, one polyamide polymer resulted which can be considered an expl and is presented below:

The Polyamide Polymer of 4,4-Dinitro-1,7-Heptanediyl Chloride and 3,3-Dinitro-1,5-Pentanediamine.

\[
\begin{array}{cccc}
O & NO_2 & \text{H} & \text{NO}_2 & \text{H} \\
\text{C(CH}_2\text{)}_2\text{-C(CH}_2\text{)}_2\text{-C-N(C(H}_2\text{))}_2\text{-C(CH}_2\text{)}_2\text{-N} & \text{NO}_2 & \text{NO}_2 \\
\end{array}
\]

\text{mw} 2600, N 20.6\%, OB to \text{CO}_2 \text{ } -90.56\%, yellow powder or mahogany-colored solid, mp 80-85\%. \text{ Sol in acet, dioxane, tetrahydrofuran and dimethylformamide, d sol in chl}. The polymer is prepd using anhydr Na succinimide as one of the monomers; liberating the pentadiamine in reaction. Using the succinimide, equivalent amounts of the monomers (56g total wt) are added to 250ml dioxane with stirring. The temp is kept at 30\° for 3 days. The soln is filtered and then poured into ice w. The product is vacuum steam distd from the ice w-dioxane soln.

The polyamide has a Q\text{c} of 3880cal/g (Ref liq H_2O at 25\°). The impact sensy at the 50\% point is 55-60cm using a BM machine with a 2kg wt (RDX, 28cm). The polyamide polymer is stable in storage at RT. Thermal stability at 65.5\° shows no failure in 5 hrs using a 1.3g sample and K1-Starch indicator paper (Ref NC, 10 min, no color); at 134.5\° using a 2.5g sample with Methyl violet indicator paper, no failure is shown after 80 min (Ref NC, 30min, no color) Ref: M.H. Gold et al, "Research in Nitro Polymers and Their Application To Solid Smokeless Propellants", Report No 482, Aeroljet Engineering Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 Dec 1950), 45, 48, 52; appendix, 9 to 12

Glycidyl 4,4,4-Trinitrobutyrate Polymer. Monomer.

Glycidyl 4,4,4-Trinitrobutyrate.
(O₂N)₃.C.(CH₂)₂.C(O)₂.CH₂.C.H₃

mw 279.19, N 15.04%, OB to CO₂ -54.44%,
light yellow, clear, viscous liq, mp -12° to
-14°, d 1.464g/cc, RI 1.4750 at 25°. Miscible
with acet and toluene. The preparation of the monomer
requires three steps, viz; 1) esterification of pro-
penoic acid with allyl alcohol yielding allyl-
propionate, 2) formation of 3,3-trinitropropyl-
propionate by double bond addition using K tri-
trimethyl in sulfuric acid medium, and 3) for-
mation of the monomer from the trinitro product
of step 2 using perbenzoic acid.

The monomer can be readily depolymerized
by concs as low as 1% NaOH. Compatible
with NC from 20-80% compd/80-20% NC and
with rubber from 30-50% compd/50-20% rubber.

The monomer has a Qₑ of 2999cal/g at 25°
(Ref liq H₂O): Qₑ -128kg cal at 25°. Impact
sensivity using a BM machine and a 2kg wt is 100cm
at the 50% all-fire point (RDX, 34cm). Thermal
stability at 65.5° using a 1.3g sample and KI-
Starch paper showed no color in 5 hrs (Ref NC,
10 min, no color); at 134.5° methyl violet paper
colored in 34 min and the sample exploded in 64
min (Ref NC, 30 min, no color).

Polymer

[(NO₃)₃.C.(CH₂)₂.CO₂.CH₂.CH₂.O-]₃ (approx.),
mw about 1500, brittle solid, mp 40-45°. Sol in
ethylene dichloride. Prepn of the polymer re-
quires that SnCl₄ (0.5 mole %) dissolved in
anhydrous ethylene chloride be added dropwise
with stirring to a -2° soln of the monomer
(25 mole %) in ethylene dichloride. After 5
days the solvent is evaporated off at 60°
and 2 microns press. The product is then treated
with activated alumina, the SnCl₄ neutralized with
Na bicarbonate and the product filtered off.

The polymer has an impact sensivity using a BM
machine and a 2kg wt of 40cm at the 50% point
(RDX, 34cm). Thermal stability at 65.5°
(KI-starch paper) was unchanged after 2 hrs
(Ref NC, 10 min, no change); at 134.5° the
sample ignited after 15 min (Ref NC, 30 min,
no color with methyl violet paper).

Toxicity. Unknown, but should be hazardous
considering other glycidyl compds.

Refs: 1) P.J. Blatz et al., "Research in Nitro
Polymers and Their Application to Solid Smoke-
less Propellants", Report No 622, Aerojet Energy
Corp, Azusa, Calif, ONR Contract N7 onr-462,
Task Order I, (26 June 1952), 41, 42, appendix
14  2) Sax (1968), 797

1-Nitro-Butyne Polymer.

Monomer

1-Nitro-Butyne (-1).

to CO₂ -137.24%, red, sticky, odiferous oil.
Prepn from 1-bromo-1-nitro-buten(-1) by re-
acting with methylene in ethanol.
The monomer exspnds when heated

Polymer

1-Nitro-Butyne(-1) Polymer.

[(CH₃.C₂H₆.C.C.NO₂)ₙ] , mw (99.10)ₙ. Prepn by
allowing the monomer to react with air at RT
for a short time

Emits dangerous fumes on decompn

Refs: 1) Beil 1, (925) 2) J. Loevenich et al,
Ber 83 (1930), 642 & CA 24, 3211 (1930)

Of the many nitro polymers developed as propellants by the Aerojet General Corp, one
polymer polymer resulted which can be con-
sidered an expl and is presented below:

The Polyester Polymer of 4,4-Dinitro-1,7-
Heptanediol Chloride and 2,2-Dinitro-1,3-
Propanedioic.

\[
\begin{bmatrix}
O & NO₂ & \text{(approx)} \\
\text{\text{-C.(CH₂)₂.C.(CH₂)₂.C.O.CH₂.C.H₂.O-}} & NO₂ & NO₂
\end{bmatrix}
\]

mw 4000-9000, N 14.74%, OB to CO₂
-58.91%, yellow powder, mp 180-185°.
Sol in dimethyl formamide; sl sol in acet, di-
oxane and tetrahydrofuran; v sl sol in chlf.
The polymer is prepd by dissolving equivalent
amounts of the monomers in dioxane followed
by maintaining the temp at 30° for 3 days. The
sln is then filtered, poured into ice w and vacuum
steam distd to obtain the product.
The polymer has a Qₑ of 2970cal/g (Ref
liq H₂O at 25°); a Qₑ of -222kg cal at 25°.
The impact sensivity at the 50% point is 85-95cm
using a BM machine with a 2kg wt (RDX, 28cm).
The polyester is stable in storage at RT. The thermal stability at 65.5° using a 1.3g sample and KI-Starch indicator paper is failure after 100 mins (Ref NC, 10 min, no color); at 134.5° using a 2.5g sample and Methyl violet paper, failure is shown after 80 mins (Ref NC, 30 mins, no color).

Ref: M.H. Gold et al, “Research in Nitro Polymers and Their Application to Solid Smokeless Propellants”, Report No 482, Aerojet Engrg Corp, Azusa, Calif, ONR contract N7 onr-462, Task Order I (15 Dec 1950), 45, appendix 5 to 8

Nitro Ethylene Polymer. See Vol 6, E229-R to E230-L

α-Chloro-α-Nitro-Ethylene Polymer

Monomer

1-Chlor-1-Nitro-Ethane (α-Chloro-α-Nitro-Ethylene). CH₂Cl.CNO₂, mw 109.50, N 12.79%, OB to CO₂ -43.84%, blk oil, bp 149–151°. Prepn from β-chloro-β-nitro ethyl-alcohol and P₂O₅ by gently heating the reactants to 170°

Polymer

α-Chloro-α-nitro-Ethylene Polymer.

[CH₂Cl.CNO₂]ₙ, mw (109.50)ₙ, yel amorph flakes, mp 126–130° (decomp). V sol in alc, ether, chl and ligr; sol in dil acetic acid; insol in w. Prepn by reacting with N carbonate soln at RT

The chloro-nitro-ethylene polymer expds when heated over an open flame

Emits dangerous fumes on decomp

Refs: 1) Beil 1, [166] 2) Sax (1968), 961

Ethylene Glycol Dinitrated Polymers. See Vol 6, E278-R to E279-L

Ethylene Glycol Polymers Nitrated. See Vol 6, E279-R to E280-L

Nitroindene Polymer

The polymer is made from indene and then nitrated

Monomer

Indene (Indonaphthen). C₉H₈, mw 116.16, OB to CO₂ -303.03%, light yel, cryst, mp -1.8 to -1.5°, bp 182.6°, d 0.996g/cc at 20/4°, RI 1.5768 at 20°. V sol in alc and eth, sol in acet, benz, py & CS₂. Prepn by fractional distn of coal tar fractions at 20mm with further purification by cooling and cryst out the indene

Indene can be detd by elution chromatography, gas chromatography, and polarographic techniques (Ref 6)

Uses. Indene monomer is used as a food additive and to form the Polymer

Polymer

mw > 3000, pale yel resin, mp 250°, d 1.10–1.15g/cc, RI 1.63–1.64 at 25°. Sol in acet, hot CCl₄ and benz. Prepn is accomplished by reacting pure indene dissolved in boiling CCl₄ (61°) with SnCl₄ as the catalyst. The polymer is pptd with alc. On being heated under pressure indene polymerizes slowly up to 175°, then the reaction becomes expl (Ref 6). Qpoly 15000 cal/mole

Indene polymer can be identified from IR spectra and the indene picrate which melts at 98°; a pink color is imparted to a CCl₄ soln of the indene polymer by SbCl₅ (Ref 6)

Besides its usage in foods, indene polymer is used in the coatings industry, inks, floorings and in rubber applications. Some use has been made of the nitrated polymer as an ingredient in fuze powder (substituting for charcoal), but because of the sensy to impact this use is discontinued (Ref 3)
Nitro indene polymer.

\[
\text{N} \quad \text{O}_2 \text{N} \\
\text{NO}_3(?) \\
\text{MW} \geq 3000, \text{N} 8.69 \text{ or } 13.53\%, \text{OB to CO}_2 \\
-188.63\% \text{ or } -332.35\% \text{ (depending on the number of NO}_2 \text{ groups per polymer unit)}, \text{brn amorph solid, mp } 230\degree \text{C. Insol in ordinary solvents. Prepn of nitroindene is presented in Classified Brit Ordn Board Proceedings such as Ref 2.}
\]

Exptl temp is above 360\degree. Impact senss is 50cm using a BM machine. Hygr test at 90% RH showed gain of 0.88%, and at 100% RH a gain of 1.61% was demonstrated. The International Heat Test at 75\degree showed a 1.1% loss of wt. Stability testing at 135\degree for 300 mins showed no acidity or expln. Vacuum stability; a 5g sample yielded 12cc of gas in 48 hrs (Ref 3).

Nitroindene was considered for use in the USAM54 Time Fuze but was found to be too sensitive to impact (Ref 3).


Dinitropolystyrene. An expl weaker than DNT (Ref 2). Prepd from the polystyrene polymer by nitrilation. It is not possible to prepare the expl by nitrilation of styrene following by polymerization (Ref 4).

Monomer.

Styrene (Phenyl Ethylene, Ethynylbenzene or Vinylbenzene).

\[
\text{CH} = \text{CH}_2, \text{mw } 104.16, \\
\text{OB to } \text{CO}_2 \text{ 307.22\%, colorl oil, mp } -30.63\degree, \\
\text{bp } 145.2\degree, \text{d } 0.9060g/cc \text{ at } 20/4\degree; \text{RI } 1.5468. \\
\text{V sol in benz and petr eth; sol in alc, eth, acet, methanol and CS}_2. \text{ Styrene occurs naturally in Styraex resin or as a by-product from water-gas pyrolysis. It can also be prepd by the reaction of benz and acetylene in the presence of Al chloride or by the dehydrogenation of ethylbenzene, which is the principal method currently used (Ref 8).}
\]

Expl limits of styrene in air are 1.1 to 6.1\% at 30\degree; Fire point (Tag open cup) is 94\degree F. Styrene polymerizes exothermally at above RT conditions. A run-away polymerization can be expld.

Gas chromatography and fp measurements are the currently used procedures for styrene detn which are accurate within 0.05\% (Ref 9).

Exposure to over 2000ppm of styrene can cause anesthesia; 10000ppm for 30–60 mins is dangerous. (Ref 9).

Styrene is used primarily to provide the polymer resin, polystyrene.

A Mil Spec, MIL-S-14195A (Ref 6a), covers the USA military requirement for styrene.

Polymer

\[
\text{[CH}_2 \text{CH}_2 \text{]n} \\
\text{MW} \geq 38000–600000, \text{colorl, amorph or crys,} \\
\text{mp } 240–250\degree, \text{d (amorph) } 1.04–1.065g/cc; \text{RI } 1.59–1.60. \text{ Sol in } \text{CCl}_4, \text{et benz, toly, et acet,} \\
\text{benz, methyl et ketone, chlf, tetrahydrofuran,} \\
\text{methyl isobutyl ketone, methylene chloride,} \\
\text{o-dichlorobenz, py and cyclohexane. Styrene polymer can be prepd in many ways. The simplest procedure is that of heating the pure monomer. The general reaction can be represented as:} \\
\text{n } \text{CH}_2 \text{CH}_2 \rightarrow (\text{-CH}_2 \text{CH}_2 \text{-}) \text{n} \\
\text{C}_6 \text{H}_5 \\
\text{C}_6 \text{H}_5 \\
\text{At } 140\degree, \text{over 90\% conversion can be obtained} \\
\text{in a few mins; at } 80\degree, \text{30\% conversion requires} \\
\text{over 90 hrs. Commercially, styrene is polymerized by either suspending it in w as a} \\
\text{carrier with stabilizing agents plus catalysts to enhance the reaction rate, or by using w with} \\
\text{emulsifying agents to give extremely small particles. In both processes a combination of two or more initiators such as benzoyl peroxide} \\
\text{and tert-butyl hydroperoxide are used with a} \\
\text{programmed reaction temp.} \\
\text{The Laboratory prepn for amorph styrene} \\
\text{involves thermal conditions or the use of butyl-lithium at } 50\degree. \text{ Crystalline polystyrene can be}
\]
prepd by using butyllithium at 0°

Dynamic differential thermal analysis is used to measure the phase transitions of the polymer. IR is used to determine the degree of unsaturation in the polymer. Monitoring of the purity and mw is done commercially using gas phase chromatography for fractionization and RI with UV absorption at 260 nanometers for poly- styrene identification and measurement.

Polystyrene is one of the most widely used plastics because of fabrication ease and the wide spectrum of properties possible. Industries using styrene-based plastics are: packaging, appliance, construction, automotive, radio and television, furniture, toy, houseware and baggage. Styrene is also used by the military as a binder in expls and rocket proplnts.

**Dinitropolystyrene (Nitropolystyrene).**

\[
\begin{array}{c}
\text{NO}_2 \\
\text{CH}_2\text{CH}_2
\end{array}
\]  

\(200\) (approx), mw \(\geq 38000\), N 14.81%, OB to CO\(_2\) -126.88%, mp > 260°, d 0.25g/cc. Sol in 90% nitric ac, DNT, NG, nitrobenz and cyclohexanone. Prepn is by nitration of isotactic polystyrene with an anhydr mixt of HNO\(_3\)/H\(_2\)SO\(_4\)/SO\(_3\) in the ratio of 4.51/2/1 at 15–20° for a few mins, heating to 50–55° for 2 hrs, followed by cooling to 25°. A yield of 33% of the w washed and dried nitropolystyrene is obtd.

Nitropolystyrene burns without melting. When confined in steel tubing of 36–42mm diam, at a d of 0.25g/cc, and driven by PA, a deton vel of 1510m/sec is obtd. No expls are obtd using a 10kg wt at 300cm on nitropolystyrene of 0.162g/cc d. Lead block expansion for a mixt of 5g of nitropolystyrene and 5g Hexogen (RDX) is 293cc (PA=295cc).

Nitropolystyrene has been suggested for use in mining. Of the more than several expl formulations developed for such a purpose one is presented here as an example: Nitropolystyrene 7.2, DNT 10.8 and Penthrite 82.0%. With a d of 1.58g/cc the deton vel of this expl compn is 7520m/sec.


Of the many nitropolymers devised as proplnts by Aerojet General Corp, one regular and one post nitratd polyurea polymer resulted which can be considered expls and are presented below:

**The Polyurea Polymer of 3,3-Dinitro-1,5-Pentane Disocyanate and 3,3-Dinitro-1,5-Pentanediadine.**

\[
\begin{array}{c}
\text{H} \\
\text{NO}_2 \\
\text{O} \\
\text{N},\text{N}(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{N},\text{C},\text{N}(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{N}\text{CH} \\
\text{NO}_2 \\
\text{O}
\end{array}
\]  

\(16\) (approx)

mw 7000, N 25.68%, OB to CO\(_2\) -87.99%, white powd or translucent grn solid, mp 110–115°. Sol in acet, tetrahydrofur and dimethylformamide; sl sol in dioxane; v sl sol in chlf. The polyurea is prepd by dissolving equivalent amounts of the monomers (80g total wt) in dimethylformamide. Using separate solns, 125ml of the disocyanate is slowly added to 120ml of the amine soln while keeping the temp below 20°. After standing 18 days at RT, most of the dimethylformamide is vacuum evapd at 50° and the syrupy residue is kept at 50° for 48 hrs. Acet dlmn is followed by filtration, then pptn in ice w. The product is vacuum steam distd at 30°; then dried over P\(_2\)O\(_5\).

The nitro polyurea has a Q\(_c\) of 3740cal/g (Ref qf H\(_2\)O at 25°), a Q\(_c\) of -181kg cal at 25°; an impact sensy at the 50% point of 80–85cm using a BM machine with a 2kg wt (RDX, 28cm). The thermal stability at 64.5° showed no failure in 5 hrs (Ref NC, 10 mins, no color) using a 1.3g sample with KI-Starch indicator paper; at 134.5° a failure after 75 mins is shown.
using a 2.5g sample and Methyl violet paper (Ref NC, 30 mins, no color)
Ref: M.H. Gold et al, “Research in Nitro Polymers and Their Application To Solid Smokeless Propellants”, Report No 482, Aerojet Engrg Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 Dec 1950), 47, 48; Appendix 13 to 16

The Post Nitratred Polyeure Polyure of 3-Nitro-3-Aza-1,5-Pentane Disocyanate and Water.

\[
\begin{align*}
O & NO_2 \\
NO_2 & H \hspace{1cm} O & NO_2 \\
-\cdot C,\cdot N,\cdot CH_2, -N,\cdot CH_2, -N,\cdot C,\cdot N,\cdot CH_2, -N,\cdot CH_2, -N,\cdot CH_2, & \quad H \\
\end{align*}
\]

mw (438.38)\(_n\), N 31.96%, OB to CO\(_2\) -69.35%, amorph solid, mp 80-90°. Sol in acet and dimethylformamide.

The initial polymer is prep'd by dropwise addn over a 30 min period of a soln of 1.0 equiv wt of the disocyanate in abs dimethylformamide to 0.50 equiv wt of w in abs dimethylformamide while maintaining a temp of 60-70°. The reaction mixt is heated to 80-90° for 1 hr and then kept at 50° for 24 hrs. The crystalline polymer (98% yield) is ground with acet, acetic acid, and vacuum dried. Post nitration is performed by soln in 100% nitric acid at RT using a ratio of 1.0g polyurea to 20ml acid. Pptn in ice w followed by vacuum drying produces a 90% yield

The post nitratred polyurea has a Qc of 3245 cal/g (Ref liq H\(_2\)O at 25°), an impact sensy of 60cm (at the 50% point) using a BM machine with 2kg wt (RDX, 28cm), a storage stability of no apparent decompn within 4 weeks at RT and a rel visc using a 1% soln in dimethylformamide of 1.11 centipoises at 25°

Presented next below are the polyurethanes, which were originally designed by Aerojet-General Corp as proplnts but may be considered expls. These entries are subdivided into polymerized compds and post polymerization nitratred compds

The Polymethane Polymer of 3,3-Dinitro-1,5-Pentane Disocyanate and 5,5-Dinitro-1,2-Hexanediol.

\[
\begin{align*}
O & NO_2 \\
NO_2 & O \\
-\cdot C,\cdot CH_2, -CH_2, -C,\cdot NO_2, -\cdot CH_2, -C,\cdot NO_2, -\cdot CH_3 & \quad O \\
C & CH_2 & NO_2 & \quad CH_3 \\
\end{align*}
\]

mw (542.39)\(_n\), N 20.66%, OB to CO\(_2\) -56.05%, amorph powder, mp 55-65°. Sol in acet. The polymer is prep'd in w, w washed, and vacuum dried over P\(_2\)O\(_5\), 2) nitratred of the polymer is accomplished using 100% nitric acid at 0°. The washed and dried yield is 97%

The polymer’s Qc is 2996cal/g at 25° (Ref liq H\(_2\)O at 25°). Impact sensy using the BM machine with a 2kg wt is 100cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° using KI-Starch paper is 23 min (Ref NC, 10 mins, no color); thermal stability at 134.5° using Methyl violet paper shows no failure in 5 hrs (Ref NC, 30 mins, no color)

The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Disocyanate and 2,2-Dinitro-1,3-Propanediol.

\[
\begin{align*}
O & NO_2 \\
NO_2 & O \\
-\cdot C,\cdot NH, -\cdot CH_2, -CH_2, -C,\cdot NO_2, -\cdot CH_2, -CH_2, -O, -\cdot NO_2 \\
-\cdot C,\cdot NH, -\cdot CH_2, -CH_2, -C,\cdot NO_2, -\cdot CH_2, -CH_2, -O, -\cdot NO_2 \\
\end{align*}
\]

mw (410.30)\(_n\), N 20.49%, OB to CO\(_2\) -58.49%, amorph solid, mp 75-78°, d 1.57g/cc. Sol in acet and dioxane. The polymer is prep'd by adding a soln of the diol and 0.05% of ferric acetylacetonate catalyst dropwise to a dioxane soln of an equiv amt of the disocyanate over a period of 1 hr. Polymerization requires 408 hrs to complete at 50°. The yield is then distilled with dioxane, pptd in w and vacuum dried
The nitro polymer has a deton rate of 6200 m/sec, a Qc of 2880cal/g (Ref liq H\(_2\)O at 25°),
an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a power by Bal Mortar of 90 (TNT=100), a thermal stability at 65.5° of over 300 mins using a 1.3g sample with KI-Starch paper as indicator (Ref NC, 10 mins, no color), a thermal stability at 134.5° of 195 mins using Methyl violet paper (Ref NC, 30 mins, no color), and a rel visc of 1.8 centipoises using a 1% soln in acet


The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

\[
\begin{align*}
\text{O} & \quad \text{NO}_2 \\
\text{–C.NH.}(\text{CH}_2)_2\text{C.} & \quad \text{O} \quad \text{NO}_2 \\
\text{C.} & \quad \text{CH}_2\text{C.NH.C.O.CH.}(\text{CH}_2)_3\text{C(NO}_2)_3
\end{align*}
\]

mw (58.36)N, N 21.21%, OB to CO\textsubscript{2} -48.45%, amorph solid, mp 70-80°, d 1.649/cm. Sol in acet.

The polymer is prepd by adding dropwise to an equiv amount of the diol dissolved in anhy dioxane, the diisocyanate plus 5x10\textsuperscript{4} mole of ferric acetylacetionate catalyst. The polymerization requires 360 hrs to complete while keeping the mix at 20-25°. After ppn in w the polymer is vacuum dried.

The polymer has a Q\textsubscript{C} of 2756cal/g (Ref liq H\textsubscript{2}O at 25°), an impact sensy of 85-85cm at the 50% point using a 2kg wt with a BM machine (RDX, 28cm), a thermal stability at 65.5° of 12 mins using a 1.3g sample and KI-Starch indicating paper (Ref NC, 10 mins, no color), a thermal stability at 134.5° of 13 mins using Methyl violet indicating paper (Ref NC, 30 mins, no color), and a rel visc of 1.64 centipoises using a 1% acet soln


The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 4,4,6,8,8-Pentamido-1,11-Decanediol.

\[
\begin{align*}
\text{O} & \quad \text{NO}_2 \\
\text{–O.}(\text{CH}_2)_3\text{C(NO}_2)_2 & \quad \text{CH}_2\text{C.CH.CH}_2\text{C(NO}_2)_2
\end{align*}
\]

The Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 4,4,6,6,8,8-Hexanitro-1,11-Undecanediol,

\[
\text{OH} \quad \text{O} \\
\begin{array}{c}
\text{O} \\
\text{(CH}_2\text{)}_2\text{C(NO}_2\text{)}_2\text{.CH}_2\text{C(NO}_2\text{)}_2\text{.CH}_2\text{O.C.N.}
\end{array}
\]

mw (702.54)_n, N 19.94%, OB to CO\textsubscript{2} -66.05%, light yellow amorphous powder, mp 40°, d 1.551g/cc. V sl sol in w and toluene; approaches miscibility with acet. The polymer is prep by dissolving mol equiv wts of the monomers in anhydioxane together with 1.5 mol equiv wt % of BF\textsubscript{3} ethereal as a catalyst. The soln is maintained at 40–50° for several weeks. The product is then pptd in w and steam distilled to remove solvent.

The nitro polymer is compatible with both NC and rubber in wt % ratios of from 20–80%. The Q\textsubscript{c} is 3323cal/g at 25° (Ref liq H\textsubscript{2}O). The Q\textsubscript{p} is 2772kg cal at 25°. Impact sensy using a BM machine with a 2kg wt is over 100cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° using a 1.3g sample colored KI-Starch paper in 8 mins (Ref NC, 10 mins, no color); at 134.5° the sample colored Methyl violet paper and expld in 8 mins (Ref NC, 30 mins, no color)


The Polymethane Polymer of 3,3-Dinitro-1,5-Pentane Diisocyanate and 5,7,9-Trinitro-5,7,9-Triaza-3,11-Dioxo-1,13-Tridecanediol.

\[
\begin{array}{cccc}
\text{NO}_2 & \text{NO}_2 & \text{NO}_2 & \text{O} \\
-\text{O.(CH}_2\text{)}_2\text{O.CH}_2\text{N.CH}_2\text{N.CH}_2\text{N.CH}_2\text{O.C.} \\
\text{H} & \text{NO}_2 & \text{H} & \text{O} \\
\text{N(CH}_2\text{)}_2\text{C.(CH}_2\text{)}_2\text{N.C.} & \text{O}_2 \quad \text{appr}
\end{array}
\]

mw 7000–9000, N 23.25%, OB to CO\textsubscript{2} -71.70%, white transparent solid, mp 55–60°. Sol in acet, dioxane, tetrahydrofuran and dimethylformamide.

The nitropolymer is prep by placing equiv amts of the monomers in dimethylformamide soln and maintaining the temp for 28 hrs at 30°. The white granular polymer is pptd in ice w, steam dist, filtered and vacuum dried. The yield is 43.92%

The nitropolymer has a Q\textsubscript{c} of 3330cal/g (Ref liq H\textsubscript{2}O at 25°), a Q\textsubscript{p} of -281 kg cal, an impact sensy of 80–85cm at the 50% point (RDX, 28cm). The thermal stability at 65.5° is no failure in 5 hrs using a 1.3g sample and KI-Starch indicator paper (Ref NC, 10 mins, no color); at 134.5° there is no failure in 5 hrs using a 2.5g sample and Methyl violet indicator paper (Ref NC, 30 mins, no color)

Ref: M.H. Gold et al., “Research In Nitro Polymers and Their Application To Solid Smokeless Propellants”, Report No 482, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 onr-462, Task Order I (15 Dec 1950), 38, 49, 50; appendix 17–20

The Polyurethane Polymer of 3,3,5,7,7-Pentanitro-1,9-Nonane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.
\[
\begin{align*}
-OCH_2.C(NO_2)_2.CH_2.C(O)_2.NH(CH_2)_2.C(NO_2)_2. \\
\text{CH}_2.N.(NO_2)_2.CH_2.C(NO_2)_2.CH_2.NH.C- \quad \text{O} \\
\end{align*}
\]

\[\text{MW (601.42) } N \text{ 20.97%, OB to CO}_2 \text{ -51.88%, yel amorph powder, mp 85-90°, d 1.560/g/cc.}
\]

V al sol in toluene; almost miscible with acet. The polymer is prepd by dissolving mol equiv amts of the monomers in anhyd dioxane and adding 1.5 mol equiv % of BF_3 etherate, and keeping the mixt at 50° for several weeks. Water pptn and steam distn produces the polymer.

The nitro polymer is compatible with NC and rubber from 20 to 80 wt %. The Q_c is 2887cal/g at 25° (liq H_2O ref). The Q_f is -253 kg cal at 25°. Impact sensy using a BM machine with a 2kg wt is 78cm at the 50% point (RDX, 28cm). Thermal stability at 65.5° using a 1.3g sample with KI-Starch paper showed color in 10 mins (Ref NC, 10 mins, no color) and at 134.5° the Methyl violet paper showed color in 7 mins; however, the sample expld in 29 mins.


The Polyurethane Polymer of 3,3,5,7,7-Penta-nitro-5-Aza-1,9-Nonane Disiocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

\[
\begin{align*}
&\text{Q} &\text{NO}_2 &\text{NO}_2 &\text{NO}_2 \\
&\text{O} &\text{NH} &\text{(CH}_2)_2 &\text{C_2.CH}_2.N &\text{C.CH}_2.C(CH_2)_2. \\
&\text{NO}_2 &\text{NO}_2 &\text{O} &\text{NH.C.O.CH}_2.C.CH_2.O- \\
&\text{NO}_2 &\text{NO}_2 &\text{N} &\text{n}
\end{align*}
\]

\[\text{MW (696.68) } N \text{ 22.81%, OB to CO}_2 \text{ -47.08%, amorph solid, mp 65-75°. Sol in acet.}
\]

The polymer is prepd by dissolving equiv amts of the monomers in abs dioxane in the ratio of 1g/ml plus 0.03% of ferric acetylacetonate catalyst, and maintaining the temp of the mixt at 30° for 50 hrs.

The polymer has a Q_c of 2954cal/g avg (Ref liq H_2O at 25°) an impact sensy of 65cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 20 mins using a 1.3g sample and KI-Starch paper as the indicator (Ref NC, 10 mins, no color); and a rel visc of 1.18 centipoises at 25° using a 1% acet soln.

Ref: P.J. Blatz et al, "Research In Nitropolymer and Their Application To Solid Smokeless Propellants", Report No 907, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 onr-462, Task Order I and Contract NO as 54-399-C.

The Polyurethane Polymer of 3,3,5,7,7-Penta-nitro-5-Aza-1,9-Nonane Disiocyanate and 2,2-Dinitro-1,3-Propanediol.
[-O.CH₂.C(NO₂)₂.CH₂.C(=O)₂.NH.(CH₂)₂.C(NO₂)₂.
CH₂.N(NO₂).CH₂.C(NO₂)₂.CH₂.NH.C---n]

mw (602.45)ₙ, N 23.26%, OB to CO₂ -45.15%, amorph solid, mp 75—85°. Sol in acet, dimethylformamide and dioxide. Prepn by dropwise addition of a hot, anhyd dioxide soln of the diisocyanate monomer to a dioxide soln of the propanediol monomer with ferric acetylacetonate catalyst, and maintaining a 50° temp for one week. During this time a 2.8% excess of the diisocyanate monomer is added in small increments. After acet dilution the polymer is pptd in w. A 95% yield is obt.

Polymers impact sensy is 40cm using a 2kg wt at the 50% point (RDX, 28cm)


The Polyurethane Polymer of 2-Nitro-2-Aza-1,4-Butane Disiocyanate and 5,5-Dinitro-1,2-Hexanediol.

[-O.NO₂ O
−C.NH.CH₂.N(CH₂)₂.NH.C.O.CH₂.CH₂.O
−(CH₂)₂
C(NO₂)₂
CH₃]n

mw (394.35)ₙ, N 21.32%, OB to CO₂ -85.20%, amorph solid, mp 70—80°. Sol in acet, butyro lactone and dimethylformamide. The polymer is prepd by dissolving equal quantities of the monomers in abs dioxide in a 1g/1ml ratio plus 0.13% of ferric acetylacetonate catalyst and maintaining a temp of 50° for 117 hrs. The product is then dissolved in dimethylformamide and pptd in stirred ice w. The yield is 96.3%.

The polymer has a Qₐ of 3571cal/g (Ref liq H₂O at 25°), an impact sensy of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of greater than 6.5 hrs using a 1.3g sample and KI-Starch paper as an indicator (Ref NC, 10 mins, no color), and a rel visc in acet (1% soln) of 1.10 centipoises at 25°


The Polyurethane Polymer of 2-Nitro-1,4-Butane Disiocyanate and 5,5,5-Triniitro-1,2-Pentaanediol.

[-O.NO₂ O
−C.NH.CH₂.N(CH₂)₂.NH.C.O.CH₂.CH.(CH₂)₂.C(NO₂)₃]n

mw (425.32)ₙ, N 23.06%, OB to CO₂ -58.31%, amorph solid, mp 80—90°. Sol in acet, butyro-
lactone and dimethylformamide. The polymer is prepared by adding a dioxane soln of 28.14g diisocyanate dropwise to a soln of 35.16g of diol and 0.0522g ferric acetylatedonate in dioxane, while the temp is maintained at 30–40°C. The polymerization requires 51 hrs to complete at 50°C. The yield is 95%

The polymer has a Q_{c} of 2931cal/g (Ref liq H_{2}O at 25°C), an impact sen of 55cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5°C, using a 1.3g sample with KI-Starch paper, of a color change at 38 mins and a failure at 2 hrs (Ref NC, 10 mins, no color), and a rel visc of 1.22 centipoises using a 1% acot soln at 25°C. Ref: P.J. Blatz et al. “Research in Nitropolymer And Their Application To Solid Smokeless Propellants”, Report No 807, Aerojet-General, Azusa, Calif, ONR Contract N7 ontr-462, Task Order I, Contract NOas 53-618-C (13 April 1954), 17

The Polymethane Polymer of 2,5-Dinitrazo-1,6-Hexane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.

\[
\begin{array}{cccc}
\text{O} & \text{NO}_2 & \text{NO}_2 & \text{O} \\
\text{C.NH.CH}_2.N.(CH)_2.N.CH_2.NH.C.O.CH_2.C.CH_2.O- \text{NO}_2 & \\
n & \\
\end{array}
\]

\[n\]

mmw (426.31)_{n}, N 26.29%, OB to CO_{2} -48.79%, amorph solid, mp 85–95°C. Sol in acet and dimethylformamide. The polymer is prepared by dissolving equal quantities of the monomers in acet in a ratio of 1g/ml plus 0.03% of ferric acetylatedonate catalyst, and maintaining a temp of 30–40°C for 30 mins. The soln temp is then kept at 50°C for 66 hrs to complete the polymerization. The polymer is then pptd from soln by pouring it into rapidly stirred ice w.

The polymer has a Q_{c} of 2767 and 2827cal/g (separate values)(Ref liq H_{2}O at 25°C), an impact sen of 100cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5°C of 1.5 hrs using a 1.3g sample and KI-Starch paper as indicator (Ref NC, 10 mins, no color), and a rel visc of 1.34 centipoises at 25°C using a 1% soln in dimethylformamide. Ref: K.W. Bills et al. “Research In Nitropolymer And Their Application To Solid Smokeless Propellants”, Report No 868, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 ontr-462, Task Order I (17 Sept 1954), 29

The Polyurethane Polymer of 2,5-Dinitrazo-1,6-Hexane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

\[
\begin{array}{cccc}
\text{O} & \text{NO}_2 & \text{NO}_2 & \text{O} \\
\text{C.NH.CH}_2.N.(CH)_2.N.CH_2.NH.C.O.CH_2.CH.O- \text{NO}_2 & \\
n & \\
\end{array}
\]

\[n\]

mmw (538.96)_{n}, N 25.25%, OB to CO_{2} -48.98%, amorph solid, mp 90–100°C. Sol in acet and dimethylformamide. The polymer is prepared by dissolving equiv quantities of the monomers in abs dioxane in the ratio of 1g/ml plus 1x10^{-4} moles of ferric acetylatedonate catalyst, and maintaining the mixt at 50°C for 164 hrs. After completion of the polymerization the product is pptd in ice w and dried.

The polymer has a Q_{c} of 2942cal/g (avg) (Ref liq H_{2}O at 25°C), an impact sen of 60cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5°C of 1 hr using a 1.3g sample with KI-Starch indicator paper (Ref NC, 10 mins, no color), and a rel visc of 1.13 centipoises at 25°C using a 1% acot soln. Ref: P.J. Blatz et al. “Research In Nitropolymer And Their Application To Solid Smokeless Propellants”, Report No 907, Aerojet-General Corp, Azusa, Calif, ONR Contract N7 ontr-462, Task Order I and Contract NOas 54-399-C (15 Dec 1954), 12

The Postnitratred Polyurethane Polymer of Ethylene Diisocyanate and Ethylene Dinitramine.

\[
\begin{array}{cccc}
\text{O} & \text{NO}_2 & \text{O} \\
\text{C.N.(CH)_2.N--C.N.CH_2.CH_2.N--} \text{NO}_2 & \\
n & \\
\end{array}
\]

\[n\]

mmw (348.18)_{n}, N 32.19%, OB to CO_{2} -18.38%, white powder, mp 175°C (decompn). The initial polymer is prepared by dissolving 0.01 mole of each of the monomers in abs dioxane and heating the mixt at 80°C for 24 hrs. The product of this step is then dissolved in 100% nitric acid, the soln heated at 70°C for twenty
mins, and the nitratd product pptd with ice w, acet-eth washed, and dried


The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Disocyanate and Ethylene Glycol.

\[
\begin{array}{cccc}
\text{O} & \text{NO}_2 & \text{NO}_2 & \text{NO}_2 \\
\text{C}_3 & \text{N} & (\text{CH}_2)_2 & \text{C} & (\text{CH}_2)_2 & N & \text{C} & \text{O} & (\text{CH}_2)_2 & \text{O} & \text{O} \\
\text{NO}_2 & & & & & & & & & & & & \\
\end{array}
\]

\(n\)

\(\text{mw (348.39)N, N 21.21%, OB to CO}_2 - 55.11\%, \text{ amorph solid, mp 40-45}^\circ \text{C. Sol in acet. The initial polymer is prepd by combining the monomers in eqivalence plus 0.02% HCl in abs dioxane to give 80 wt % of the monomers in soln. Polymerization requires 746 hrs at 50}^\circ \text{C for completion. The product is obtd by acet dilution of the reaction mixt with subsequent pptn in w and vacuum drying. Post polymerization nitration is accomplished by adding 5.269 g of the polymer to 50 ml of 100% nitric acid at 0}^\circ \text{C and stirring for 30 mins. The 97% yield is obtd by pptn in ice w and vacuum drying.}

The postnitrated polymer has a \(Q_c\) of 2996 cal/g (Ref liq H\(_2\)O at 25\(^\circ\)C), an impact sensy at the 50% point of 85 cm using a BM machine with 2 kg wt (RDX, 28 cm), and a rel vsc of 1.5 centipoises at 25\(^\circ\)C using a 2% acet soln


The Postnitrated Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane Disocyanate and 5,5,5-

Trinitro-1,2-Pentanediol.

\[
\begin{array}{cccc}
\text{O} & \text{NO}_2 & \text{NO}_2 & \text{O} \\
\text{C}_3 & \text{N} & (\text{CH}_2)_2 & \text{C} & (\text{CH}_2)_2 & N & \text{C} & \text{O} & (\text{CH}_2)_3 & \text{C(NO}_2)_3 \\
\text{NO}_2 & & & & & & & & & & & \text{NO}_2 & \text{NO}_2 \\
\end{array}
\]

\(n\)

\(\text{mw (573.36)N, N 21.99%, OB to CO}_2 - 37.67\%, \text{ amorph solid, mp 50-70}^\circ \text{C. Sol in dioxane. The initial polymer is already described earlier in this article. The post polymerization nitration is accomplished by adding 250 ml of cold 100% nitric acid to 30.7 g of the initial polymer and then bringing the temp to 50}^\circ \text{C for 20 mins. Pptn in ice w and vacuum drying produces the desired product.}

The postnitrated polymer has a \(Q_c\) of 2491 cal/g (Ref liq H\(_2\)O at 25\(^\circ\)C), an impact sensy of
30 cm at the 50% point using a BM machine with a 2 kg wt (RDX, 28 cm), a thermal stability at 65.5° of 5 mins using a 1.3 g sample and KI-Starch indicator paper (Ref NC, 10 mins, no color), and a rel visc of 1.6 centipoises using a 2% dioxane soln at 25°.


The Postnitratied Polyurethane Polymer of 3,3-Dinitro-1,5-Pentane with N,N'-Bis(2-Hydroxyethyl) Oxamide.

\[
\text{O}_3\text{NO}_2 \quad \text{O}
\]
\[
-\text{C}_2\text{N}(-\text{CH}_2)_2\text{C}_2\text{O}_2\text{N}(-\text{CH}_2)_2\text{N}\cdot \text{C}_2\text{O}_2\text{N}(-\text{CH}_2)_2\text{N}.
\]
\[
\text{O}_3\text{NO}_2 \quad \text{O}
\]
\[
\text{C}_2\text{N}(-\text{CH}_2)_2\text{O}^-.
\]

\[n\]

mw (600.39) g/mol, N 23.33%, OB to CO₂ = 42.64%, white, amorph powder, mp 85–90°, d 1.66 g/cc. Sol in acet, tetrahydrofuran and eth acetate, sl sol in n-heptane and methanol; v sl sol in toluene and w. Prepn of the initial polymer is from a dioxane soln at 50° of 2.0 equiv mol wts each of the monomers using either 1.5 equiv wt % of boron trifluoride etherate or 2.0 equiv wt % of vanadyl acetylene acetate as a catalyst to enhance the polymerization rate. Complete polymerization or gel is accomplished in about 70 hrs at 50°. The reaction rate is further enhanced by the addition of 0.072 equiv wt % of the isocyanate monomer after the initial reaction, resulting in gelation after 40 hrs at 50°. The hot dioxane soluble product is w ptd, vacuum steam-distd and dried. Post polymerization nitration of the polymer is accomplished with 100% nitric acid at 65°.

The postnitratied polyurethane polymer has a Qₜ of 2531 cal/g (Ref liq H₂O at 25°), an impact senst of 75 cm at the 50% point using a BM machine with a 2 kg wt (RDX, 28 cm), a thermal stability at 65.5° of 5 mins using a 1.3 g sample and KI-Starch paper as the indicator (Ref NC, 10 mins, no color), and a rel visc of 1.19 centipoises using a 1% acet soln at 25°.

The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and Ethylene Glycol.

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 & \quad \text{O} & \quad \text{O} \\
-\text{C}.\text{N} & (\text{CH}_2)_2 & \text{N} & (\text{CH}_2)_2 & \text{N} & \text{C}.\text{O} & \text{CH}_2 & \text{CH}_2 & \text{O} & - \\
\text{NO}_2 & & & & & & & & & \\
\end{align*}
\]

\[n\]

\[\text{mw (352.26), N 23.86%, OB to CO}_2 - 54.51%, \text{amorph solid, mp 50–60°. Sol in dimethylformamide. The initial polymer is prep by cautious admixture of the monomers individually dissolved in abs dioxane in equiv proportions plus } 5 \times 10^{-4} \text{ mole of ferric acetylacetone catalyst (the total is represented by the ratio of 1 g monomers/0.65 ml dioxane). The polymerization is completed in 16 hrs at a constant temp of 50°. The 97% yield is acet dissolved, w pptd and vacuum dried. Post polymerization nitration of the polymer is accomplished by adding 200 ml of 100% nitric acid to 22.0 g of the polymer. After soln of the polymer the excess acid is vacuum distd. The 97% yield is then acet dissolved and repptd in chl. The postnitrated polymer has a Qc of 3067 cal/g (Ref leq H}_2O at 25°) an impact sensy of 90 cm at the 50% point using a BM machine with a 2 kg wt (RDX, 28 cm), a thermal stability at 65.5° of 7 min using a 1.3 g sample wt with KI-Starch indicator paper (Ref NC, 10 mins, no color) and a rel visc of 1.2 centipoises at 25° using a 1% dimethylformamide soln.


The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Diisocyanate and N,N'-Bis (2 Hydroxyethyl) Oxamide.

\[
\begin{align*}
\text{NO}_2 & \quad \text{NO}_2 & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
-\text{C}.\text{N} & (\text{CH}_2)_2 & \text{N} & (\text{CH}_2)_2 & \text{N} & \text{C}.\text{O} & (\text{CH}_2)_2 & \text{N} & \text{C}.\text{C} & (\text{CH}_2)_2 & \text{O} & - \\
\text{NO}_2 & & & & & & & & & & & \\
\text{NO}_2 & & & & & & & & & & & \\
\end{align*}
\]

\[n\]

\[\text{mw (556.38), N 25.18%, OB to CO}_2 - 46.01%, \text{amorph solid, mp 65–75°. Sol in formic acid and dimethylformamide. The initial polymer is prep by dropwise addition of a soln of the diisocyanate in abs dimethylformamide to a soln of an equiv amt of the diol together with } 5 \times 10^{-4} \text{ mole of ferric acetylacetone catalyst in abs dimethylformamide, and stirring the mixt for 4 hours at 70° until polymerization is complete. To 1.5 g of the acet-methanol-eth washed and dried product is added 250 ml of 100% nitric acid. The temp is maintained at 50–60° for 1 hr and then the acid soln is drowned in 2 liters of ice w to ppt the postnitrated polymer. The postnitrated polymer has a Qc of 2631 cal/g (Ref Leq H}_2O at 25°), an impact sensy of 47 cm at the 50% point using a BM machine with}

\[\text{N 153}\]
a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of failure in 8 mins using a 1.3g sample with KI-Starch paper (Ref NC, 10 mins, no color), and a rel visc of 1.05 centipoises (1% soln in dimethylformamide) at 25°.


The Postnitrated Polyurethane Polymer of 3-Nitroaza-1,5-Pentane Diisocyanate and 5,5,5-Trinitro-1,2-Pentaanediol.

\[
\begin{array}{c}
\text{O} \\
\text{C.N.} \text{(CH}_2\text{)}_2 \text{N(} \text{CH}_2\text{)}_2 \text{N.C.O.CH.CH}_{2\text{O}} \\
\text{NO}_2 \text{ NO}_2 \text{ NO}_2 \text{ (CH}_2\text{)}_2 \text{C(NO}_2\text{)}_3 \\
\end{array}
\]

\[n\]

\[\text{m}w (548.74)_n, \text{N} 23.82\%, \text{OB to CO}_2 -39.36\%, \text{amorph solid, mp 75–85°. Sol in acet. The initial polymer is prepd by dropwise addition of the diisocyanate in abs dioxane to a dioxane soln of an equiv amt of the diol plus 5 x 10^{-4} mole of ferric acetylacetonate catalyst, over a period of 30 mins while maintaining the temp at 40–50°. Polymerization at 50° requires 43 hrs to complete. After acyl soln and w pptn, the yield is vacuum dried. Post polymerization nitration is accomplished by soln of the polymer in 100% nitric acid at 0° in the ratio of 1 g polymer to 10ml acid. The nitration is completed upon soln of the polymer in acid. The excess nitric acid is removed at RT by vacuum distn, the polymer is dissolved in acet and pptd in methylene chloride.}

The postnitrated polymer has a \(Q_c\) of 2601 cal/g (Ref liq H\(_2\)O at 25°), an impact sens of 83cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 5 min to failure using KI-Starch paper with a 1.3g sample (Ref NC, 10 mins, no color); a 1% soln in acet has a rel visc of 1.38 centipoises at 25°.


The Postnitrated Polyurethane Polymer of 3-Nitro-3-Aza-1,5-Pentane Disiocyanate and 2-Nitro-2-Methyl-1,3-Propanediol.

\[
\begin{array}{c}
\text{O} \\
\text{N(O)CH}_2\text{(CH}_2\text{)}_2 \text{N(O)CH}_2\text{(CH}_2\text{)}_2 \text{N.C.O.CH}_2\text{CH}_2\text{O} \\
\text{NO}_2 \text{ NO}_2 \text{ NO}_2 \text{ (CH}_2\text{)}_2 \text{C(NO}_2\text{)}_3 \\
\end{array}
\]

\[n\]

\[\text{m}w (425.32)_n, \text{N} 23.06\%, \text{OB to CO}_2 -58.31\%, \text{amorph solid, mp 70–80°. Sol in acet. The initial polymer is prepd by dropwise addition of a soln of the diisocyanate in dimethylformamide to a dimethylformamide soln of an equiv wt of diol plus 1x10^{-4} mole ferric acetylacetone catalyst over a period of 15 mins. Polymerization is completed in 136 hrs at 50°. After dilution with dimethylformamide, the polymer is pptd in w and vacuum dried. Post polymerization nitration is accomplished by soln of the polymer in 100% nitric acid at 0° in the ratio of 1 g polymer to 15ml acid. Nitration is completed on soln of the polymer. The excess acid is vacuum distd at RT, the polymer is dissolved in acet and pptd in methylene chloride.}

The postnitrated polymer has a \(Q_c\) of 2994 cal/g (Ref liq H\(_2\)O at 25°), an impact sens of 83cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of 10 mins to failure using KI-Starch paper and a 1.3g sample (Ref NC, 10 mins, no color), and a rel visc at 25° of a 1% soln in acet of 1.20 centipoises.


The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate and 2,2-Dinitro-1,3-Propanediol.

\[
\begin{array}{c}
\text{O} \\
\text{N(O)CH}_2\text{(CH}_2\text{)}_2 \text{N(O)CH}_2\text{(CH}_2\text{)}_2 \text{N.C.O.CH}_2\text{CH}_2\text{O} \\
\text{NO}_2 \text{ NO}_2 \text{ NO}_2 \text{ (CH}_2\text{)}_2 \text{C(NO}_2\text{)}_3 \\
\end{array}
\]

\[n\]
The polymer has a Qc of 2979 cal/g (Ref liq H$_2$O at 25$^\circ$). Impact sens is 75 cm at the 50% point using a BM machine with a 2 kg wt (RDX, 28 cm).


The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate with 5,5-Dinitro-1,2-Hexanediol.

\[
\begin{align*}
&\text{O} & &\text{NO}_2 & &\text{NO}_2 & &\text{O} \\
&-\tilde{C}.\text{N}((\text{CH}_2)_2.\text{N}((\text{CH}_2)_2.\text{N}((\text{CH}_2)_2.\text{N}C.\text{O}((\text{CH}_2)_2.\text{O} \\
& & & & & & &\text{NO}_2 & &\text{NO}_2 & &\text{NO}_2 & &\text{H}_2\text{C}C(\text{NO}_2)_2.\text{CH}_2\text{n}
\end{align*}
\]

mw (586.46)$_n$, N 23.89%, OB to CO$_2$ — 62.75%, amorph solid, mp 85—95$^\circ$. Sol in acet and dimethylformamide. The initial polymer is prep by reacting equiv quantities of diol and diisocyanate in dioxane using 10$^3$ mole of ferric acetylactone catalyst at 50$^\circ$. The polymerization requires 186 hrs at 50$^\circ$. After w pptn and vacuum drying the 97% yield is nitrated using cold 100% nitric acid. After soin of the polymer, the product is pptd in ice-w, w washed and vacuum dried to produce a 93% yield.

The postnitrated polymer has a Qc of 3148 cal/g (Ref liq H$_2$O at 25$^\circ$) and an impact sens of 90 cm at the 50% point using a BM machine with a 2 kg wt (RDX, 28 cm).


The Postnitrated Polyurethane Polymer of 3,6-Dinitro-3,6-Diaza-1,8-Octane Diisocyanate and 5,5,5-Trinitro-1,2-Pentanediol.

\[
\begin{align*}
&\text{O} & &\text{NO}_2 & &\text{NO}_2 & &\text{O} \\
&-\tilde{C}.\text{N}((\text{CH}_2)_2.\text{N}((\text{CH}_2)_2.\text{N}((\text{CH}_2)_2.\text{N}C.\text{O}((\text{CH}_2)_2.\text{CH}_2\text{O} \\
& & & & & & &\text{NO}_2 & &\text{NO}_2 & &\text{C}(\text{NO}_2)_2\text{n}
\end{align*}
\]

mw (617.43)$_n$, N 24.96%, OB to CO$_2$ — 45.35%, amorph solid, mp 70—80$^\circ$. Sol in acet, butyrolactone and dimethylformamide. The initial
polymer is prepared by combining equivalent amounts of the monomers in abs dioxane soln together with 1x10^-3 mole of ferric acetylacetonate catalyst and maintaining the soln at 50° for 192 hrs. The polymer is then diluted with acet and pptd in w. Post polymerization nitration is accomplished by adding 400ml of 100% nitric acid at 0° to 25g of the dried polymer. When the polymer is completely dissolved, the excess acid is removed by distn at reduced press. The anhydrous dioxane-acet soln is then pptd in methylene chloride and dried.

The postnitrated polymer has a Qc of 2712 cal/g (Ref liq H2O at 25°), an impact sensy of 82cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), a thermal stability at 65.5° of failure in 3 mins using KI-Starch paper with a 1.3g sample (NC, 10 mins, no color), and a rel visc in acet of 1.23 centipoises using a 1% soln at 25°.


The Postnitrated Polyurethane Polymer of 3,6-Dinitro-1,5-Octane Diisocyanate and 2-Methyl-2-Nitro-1,3-Propanediol.

\[
\begin{align*}
\text{O} & \quad \text{NO}_2 \\
\text{O} & \quad \text{NO}_2 \\
\text{C}_2\text{N} & \quad \text{CH}_2 \quad \text{N} \quad \text{CH}_2 \quad \text{N} \quad \text{CH}_2 \quad \text{N} \quad \text{CH}_2 \quad \text{N} \quad \text{CH}_2 \quad \text{O} \\
\text{NO}_2 & \quad \text{NO}_2 \\
\text{CH}_3 & \\
\end{align*}
\]

mw (513.40)ₙ, N 24.56%, OB to CO₂ -60.77%, amorph solid, mp 55-65°. Sol in dimethylformamide. The initial polymer is prepd by dissolving equiv quantities of diol and diisocyanate in dioxane with 10^-3 mole of ferric acetylacetonate catalyst and maintaining the temp at 50° for 200 hrs. Post polymerization nitration of the polymer is accomplished by dissolving the dried polymer in cold 100% nitric acid at 0° (15g/150ml). Upon soln the excess acid is vacuum dist at RT, the product is dissolved in dimethylformamide and pptd in methylene chloride.

The postnitrated polymer has a Qc of 3102 cal/g (Ref liq H2O at 25°), an impact sensy of 50cm at the 50% point using a BM machine with a 2kg wt (RDX, 28cm), and a 65.5° thermal stability using KI-Starch paper of 12 mins to failure using a 1.3g sample (Ref NC 10 mins, no color)

Ref: P.J. Blatz et al, "Research In Nitropolymer And Their Application To Solid Smokeless Propellants", Report No 772, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 enr-462, Task Order I, Contract NO as 53-618-C (Dec 1953), 19

The Postnitrated Polyurethane Polymer of 3,6-Dinitro-1,5-Octane Diisocyanate with N,N'-Bis (2-Hydroxyethyl) Oxamide.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{N} \quad \text{O}_2 \\
\text{N} \quad \text{O}_2 & \quad \\
\text{C}_2\text{H}_4 & \quad \text{N} \quad \text{O}_2 \\
\text{H}_2\text{CO} & \quad \text{H}_2\text{CO} \\
\text{O} & \quad \text{N} \quad \text{O}_2 \\
\end{align*}
\]

mw (644.46)ₙ, N 26.09%, OB to CO₂ -49.65%, amorph solid, mp 65-70°. Sol in acet and dimethylformamide. The initial polymer is prepd by heating the monomers to 100° together with a small aml of ferric acetylacetonate catalyst (0.0001 mole/equiv monomer wt) in a solvent mixt consisting of 2/1/40 of dioxane/dimethylformamide/acet. After soln of the reactants the mixt is kept at 50° for 186 hrs. The vacuum dried polymer is then pptd in ice-w, w washed and vacuum dried. Yield rel to original monomers is 61%

The polymer has a Qc of 2799 cal/g (Ref liq H2O at 25°). Impact sensy is 90cm at the 50% point using a 2kg wt in a BM machine (RDX, 28cm)

Ref: P.J. Blatz et al, "Research In Nitropolymer And Their Application To Solid Smokeless Propellants", Report No 772, Aerojet-General Corp, Azusa, Calif; ONR Contract N7 enr-462, Task Order I, Contract NO as 53-618-C (Dec 1953), 15

Addl References on Nitropolymers. A) L.T. Carleton et al, "Research In Nitro Poly-

...
NITROSTARCH (Nitrate d’amidon in Fr; Nitrostaerke or Streakenitrat in Ger)

Nitrostarch (NS) is a nitrate ester (more properly a mixt of several nitrate esters) of starch, which is a plant-product polysaccharide of the general formula \( (\text{C}_6\text{H}_{12}\text{O}_5)_{\text{N}} \). The general molecular formula for NS is \( [\text{C}_6\text{H}_2(\text{OH})_x(\text{ONO}_2)_y]_n \), where \( x + y = 3 \). The following empirical relation, similar to that used for NC (see Vol 2, C100-R), can be employed to obtain \( y \) as a function of \( N \), the measured nitrogen content (in %) of NS:

\[
y = 162N / (1400 - 45N)
\]

For example, NS of 13.5% N contains, on the average, about 2.75 nitrate groups and about 0.25 OH group per saccharide unit and consequently consists primarily of a mixt of di- and tri-nitrates.

According to Hackel and Urbański (Ref 12), the solubility of Nitrostarch is dependent on its N content. Nitrostarch containing 8.0–12.8% N dissolves completely in eth-alc, but products with a N content of over 12.8% are only partially soluble. For 13.1% N, the solubility amounts to about 78%.

Nitrostarch characterized by a N content below 8.0% is scarcely soluble in eth-alc. Thus the solubility of a 6.4% N-product is only 8.4%.

Nitrostarch dissolves in alc more easily than NC, and at a N content of 10.0–11.5% is wholly soluble in ethyl alc. Incomplete dissolution indicates Nitrostarch of higher or lower N percentage. A product containing 12.1% N has a solubility of 32.5%.

Nitrostarch of 6.4 or higher % N dissolves completely in acet.

X-ray diffraction studies by Kolaczkowska & Urbański (Ref 13) suggest that during nitration starch passes thru a hydrolysis stage according to:

\[
\text{HNO}_3 + \text{Starch} \rightarrow \text{soluble starch} \rightarrow \text{Nitrostarch}
\]

This view is also supported by viscosity data, which show that the starch molecule is strongly degraded during nitration. The viscosity of NS solns is appreciably lower than the viscosity of corresponding NC solns. Consequently NS cannot be used in lacquer or smokeless powder production. For a thorough discussion of NS solubility and degradation see Ref 26, pp 422–26.

Nitrostarch is still used extensively by the Trojan Powder Company as the sensitizer in their “non-headache” Dynamites, where it replaces the NG/EGDN mixts used by other Dynamite manufacturers. It was used in WWI in Trojan Explosive and in Granite. The former was used as the bursting charge for hand grenades, rifle grenades, and mortar shells, and the latter only for grenades (Ref 21a). According to Urbański (Ref 26, p 420), it was still used in Hungary during WWII for filling hand grenades. It is also
the major constituent of NSX, a Nitrostarch Demolition Explosive (Ref 30).

Historical.

Extensive historical reviews of NS are given by Caesar (Ref 21a) and by Urbanski (Ref 26, pp 418–20). For the early history of NS, which parallels that of NC, we quote Urbanski:

"Braconnot, who first nitrated cellulose, was also the first to nitrate starch, in 1833 (Ref 1). He dissolved potato meal in conc nitric acid, and then precipitated the nitration product by adding water. These experiments were repeated by Pelouze (Ref 2) and Buijs Ballot (Ref 3), whereas in an experiment of Rheinsch (Ref 4) the starch was nitrated like cellulose in modern methods, by means of a mixture of nitric and sulphuric acids. For a long time nitrostarch was not distinguished from nitrocellulose. Eventually, attention was drawn to their difference by Béchamp (Ref 5). By reduction of starch nitrate he recovered the initial carbohydrate, ie, starch in a form that differed from the non-nitrated original starch by its solubility in water. (In accordance with our knowledge it was most probably dextrin). Béchamp (Ref 6) tried to apply various methods for isolating nitrostarch dissolved in nitric acid. He used both water and sulphuric acid, and obtained nitrostarch with different nitrogen contents, and has observed that the product separated by means of sulphuric acid was the less stable, readily undergoing spontaneous decomposition. Mühlnäuser (Ref 7) expressed a far-sighted view that the low stability of this nitrostarch was due to partial sulphonation brought about by sulphuric acid.

The most extensive of the researches carried out in the nineteenth century were those of Mühlnäuser (Ref 7) who dissolved starch in a ten-fold quantity of nitric acid, sp gr 1.50, and precipitated the product with thirty times as much sulphuric acid. In this way he introduced 13.5% N, but the nitration product was unstable.

Experimenting with a still stronger nitric acid, sp gr 1.52, Will and Lenze (Ref 8) prepared nitrostarch characterized by a nitrogen content of 14.04%. They established that it is possible to produce nitrostarch of high nitrogen percentage and adequate stability providing it is subjected to a stabilization boil in ethyl alcohol.

Moreover, Will and Lenze established that starch can be nitrated in a manner resembling cellulose nitration, by means of a mixture of nitric and sulphuric acid, to obtain a product containing 13.9% N. The same method was tried by Sapiroznikov (Ref 11). However, he did not wholly confirm the results published by Will and Lenze, since the maximum nitrogen content in his product was 13.5%.

Starch nitrated by Brown and Millar (Ref 10) by dissolution in nitric acid and subsequent precipitation with the help of sulphuric acid, was stabilized by washing in ether and chloroform.

Soluble starch was nitrated by Syniewski (Ref 9). The most extensive published researches devoted to the preparation, purification and properties of nitrostarch are those of Hackel and T. Urbanski (Ref 12)."

US production of NS began in 1888 under the name of Volney Powder. Improved NS stability was achieved by Hough, who operated two plants in New Jersey for the production of NS. Later (1905 to 1907) Dupont and Eastern Dynamite Corp experimented with NS expls. At about that time Trojan Powder Co became interested in NS. It soon became and still is the largest manufacturer of NS. Numerous patents (from 1918 to 1945) have been issued to W.O. Snelling (of Trojan Powder Co) for the prepn, stabilization and use of NS (Ref 21a).

At present Trojan Powder Co is the only large-scale producer of NS. Some NS was manufactured in Hungary and Poland between the two World Wars but its production is now discontinued (Ref 26, p 420)

Preparation.

Nitrostarch can be prepared by dissolving starch in an excess of nitric acid and pouring this solution into an excess of sulfuric acid to precipitate NS as an amorphous powder. This method is uneconomical and hard to control. Consequently it is not used commercially.

The usual preparative methods employ mixed acids. The N content of the NS depends on the composition of the mixed acid and on the mixed acid-to-starch ratio. This is illustrated in the triangular diagram of Fig 1 obtained by Hackel and Urbanski (Ref 12). Starch was nitrated for one hour and 50 mins at 10–12°. The acid compn is given in mole %. The region of mixts between the curve AAA'A' and the HNO₃—
Comparison of the Sapožnikov graph for NC with the graph by Hackel and Urbanski shows that in the latter the curve has a minimum which corresponds approx to a mixed acid whose nitric acid-to-sulfuric acid weight ratio is about 6 (mole ratio about 9) (See article on Nitration in this Vol)

According to Izrailashvili (Ref 18a) high NO$_2^+$conc favors production of high N-content NS

Kunz & Toth (Ref 22) found that nitration time for NS varies linearly with temp (Fig 2). Above 14°C nitration is very rapid

Nitrostarch can also be prepared via nitration with nitric and phosphoric acids (Ref 12); N$_2$O$_5$ dissolved in nitric acid (Ref 14); N$_2$O$_5$ dissolved in chloroform (Ref 18); or nitric acid with P$_2$O$_5$ (Ref 23)

Details on commercial production of NS are scarce. Davis (Ref 17) describes a mixed acid consisting of 38% HNO$_3$ and 62% H$_2$SO$_4$, with a 4 to 1 acid-to-starch ratio, and a nitration temp of 38–40°C. He states that after nitration the contents are drowned in water and the NS is separated by filtration

A two-stage nitration at 5°C is claimed to improve NS stability (Ref 15)

Stabilization.

Stabilization of NS is frequently kept as a trade secret, although there have been some recent publications (Refs 23, 24, 25, 27, & 28). Early studies (Ref 12) suggest that NS made using nitric acid is more stable than that made with mixed acid — possibly because starch sulfates are formed with the latter

Fig 2. Reaction time of nitration of starch as a function of temperature

(I) 35.0% HNO$_3$, 57.5% H$_2$SO$_4$, 7.5% H$_2$O,
(II) 33.4% HNO$_3$, 60.75% H$_2$SO$_4$, 5.81% H$_2$O
Usually, prolonged boiling in acid water and then in alkaline water is used to stabilize NS. However, there are claims that boiling with alkaline water decreases NS stability (Ref 28). However, in a previous publication (Ref 27) these same authors claim that kier-boiling or prolonged boiling in water or in dilute alkaline solution improves stability. Addition of substances such as epichlorohydrin that swell the NS and aid water penetration is claimed to improve stability (Ref 16)

**Explosive Properties.**

Smolenski & Strzondala (Ref 20) obtained the following heats of combustion and heats of formation for NS:

**Table 1**

<table>
<thead>
<tr>
<th>Nitrogen content %</th>
<th>Heat of combustion/cal</th>
<th>Heat of formation/cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.52</td>
<td>2575.8</td>
<td>702.4</td>
</tr>
<tr>
<td>11.02</td>
<td>2510.6</td>
<td>668.3</td>
</tr>
<tr>
<td>12.87</td>
<td>2276.7</td>
<td>555.5</td>
</tr>
<tr>
<td>13.24</td>
<td>2217.9</td>
<td>541.0</td>
</tr>
</tbody>
</table>

Differences in heats of formation of the two kinds of Nitrostarch are regarded by these authors as related to the presence of sulfuric esters in the Nitrostarches prepared by means of mixed acids.

Explosive properties of NS obtained by Hackel & Urban'ski (Ref 12a) are summarized in the following tabulation:

**Table 2**

<table>
<thead>
<tr>
<th>Nitrogen content %</th>
<th>Heat of combustion/cal</th>
<th>Heat of formation/cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.52</td>
<td>2580.7</td>
<td>696.5</td>
</tr>
<tr>
<td>12.20</td>
<td>2378.4</td>
<td>576.3</td>
</tr>
<tr>
<td>12.87</td>
<td>2309.0</td>
<td>523.3</td>
</tr>
<tr>
<td>13.34</td>
<td>2273.3</td>
<td>504.5</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Nitrogen content %</th>
<th>Rate of detonation, m/sec (in a pipe of diameter 34/28 mm), d = 0.88, initiation by No 8 detonator</th>
<th>Lead block test cm³</th>
<th>Sensitivity to shock; % of explosions caused by a 5-kg weight falling from a height of cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.4</td>
<td>6190</td>
<td>430</td>
<td>21</td>
</tr>
<tr>
<td>13.1</td>
<td>5740</td>
<td>395</td>
<td>23</td>
</tr>
<tr>
<td>12.8</td>
<td>5300</td>
<td>375</td>
<td></td>
</tr>
<tr>
<td>12.4</td>
<td>4950</td>
<td>360</td>
<td>36</td>
</tr>
<tr>
<td>12.1</td>
<td>4480</td>
<td>320</td>
<td>38</td>
</tr>
<tr>
<td>11.6</td>
<td>3880</td>
<td>300</td>
<td>70</td>
</tr>
<tr>
<td>11.8</td>
<td>3020</td>
<td>260</td>
<td>100</td>
</tr>
<tr>
<td>10.5</td>
<td>2880</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>9.4</td>
<td>1500</td>
<td>160</td>
<td>100</td>
</tr>
<tr>
<td>8.9</td>
<td>1000</td>
<td>125</td>
<td>100</td>
</tr>
<tr>
<td>7.7</td>
<td>does not detonate</td>
<td>35</td>
<td>does not explode</td>
</tr>
</tbody>
</table>
Le Roux (Ref 19) examined the expl properties of Nitrostarch of 13.52% N. At a density of 0.90g/cc, a charge of 30mm diam in a cardboard tube detonated at the rate of 4970m/sec. The relative lead block expansion was 117% of Picric Acid.

Cook (Ref 21) presents a thermo-hydrodynamic calc of the detonation parameters and detonation products of two NS expls containing 25/1.5/73.5 NS/Al/AN-SN dope and 27.5/3/69.5 NS/Al/AN-SN dope.

Urbański (Ref 26, p 426) states NS burns readily in a manner similar to NC.

Merzhanov and coworkers (Ref 29) studied the ignition of NS (and other expls) in a hot gas stream and found that the critical expln temp decreases with increasing O content of the gas.

**Explosive Compositions Containing NS.**

Davis (Ref 17) gives the following compn for Trojan Explosive: 23-27/31-35/36-40/1.5-2.5/0.5-1.5/0.5-1.5/0.2-0.4% NS/AN/AN/charcoal/ heavy hydrocarbon/antacid/diphenylamine. For Grenite he shows 97/1.5/1.5% NS/petroleum oil/gum arabic. He also gives examples of early Trojan NS Dynamites as follows: 30-39/0-20/37-58/0-5/0.5-0.75/2-5/1.0-1.5% NS/AN-TNT mixt/ SN/carbonaceous matter/paraffin oil/sulfur/Ca carbonate.

The Nitrostarch Demolition Explosive NSX consists of: 49/40/7/3/1% NS (12.5% N)/Ba nitrate/MNN/paranitroaniline/oil (Ref 30).

Several more recent NS expls are described below:

G.L. Griffith & D.G. Samuel, USP 2860041 (1958) & CA 53, 3697 (1959). Provides a process for preparing blasting expls that are relatively novel and nonhazardous in handling and manufacturing, but which acquire full sensitivity by the time the expl is to be used. This is accomplished thru incorporation into a mixt containing a damp, nitrated hydrocarbon such as Nitrostarch and the normal ingredients of blasting Dynamites up to about 5% of an organic hydrophobic but not hygroscopic latent sensitizer (water absorber) such as locust-bean extract, gum karaya, or Na carboxymethylcellulose. This absorbs the water from the damp NS to sensitize the mixt and in so doing forms a gelatinous layer on the particles which aids in preventing penetration of external water.

G.L. Griffith & F.W. Wells, USP 3083127 (1963) & CA 58, 13704 (1963). Higher detonation velocity, better cratering and improved ease of initiation are claimed when NS replaces TNT in the following slurry expl: 10-30% NS/35-75% AN + SN/10-40% H2O plus conventional fuels and thickeners.

F.B. Wells & W.H. Rinkenbach, USP 3180773 (1965) & CA 63, 2844 (1965). Bone meal imparts improved water resistance to the following NS Dynamite: 25% dry NS/51.6% AN/20.8% SN/2% commerical ground bone meal/0.3% ZnO/0.3% mineral oil.

G.L. Griffith, USP 3300348 & CA 66, 67518 (1967). Nonsegregating expl co-nitrates having relatively low impact sensitivities and higher rates of detonation and higher initiation sensitivities than mechanical mixts of the individual nitrates are claimed which are particularly useful as sensitizing expls. These are provided by nitration, preferably with a mixt of HNO3 and sufficient H2SO4 to inhibit soln of the nitric esters in the nitrating medium, of a mixt of a commercial starch, preferably corn starch, and a polyol or polyol derivative such as pentaerythritol (preferred), its hydroxysteres, dipentaerythritol and higher pentaerythritols, mannitol, sorbitol, erythritol, trimethylolpropane, and neopentyl glycol. The materials may be nitrated consecutively or simultaneously.

G.L. Griffith & W.L. Schwoyer, USP 3457128 (1969) & CA 71, 72517 (1969). Particulate self-explosive nitrated materials, such as Nitrostarch, PETN, TNT, and their mixts, can be made relatively safe to handle and transport thru formation of a uniform nongelled ag slurry containing 10-50% water and 0.5-10% partially hydrolyzed polyacrylamide suspending agent having 0.1-50% free acid, and ≥ 50% unhydrolyzed amide groups, and a mw of 1,000,000-25,000,000. Such slurries are especially useful for transporting expl sensitizers used in slaggy blasting agents. Thus, a mixt was prep'd by stirring together 66% dry Nitrostarch, 39.8% water, and 0.2% Polyhall 295 (a commercial partially hydrolyzed polyacrylamide of mw 3,000,000-8,000,000 containing 15-30% amide groups hydrolyzed to acid groups). This slurry showed no separation after 2 months' storage at 50-80°F, after which 50 parts of it was blended with dry AN 50, flake Al 30, and water 11 parts.
to produce an explosive slurry which, when tested in a bore hole, detonated readily and produced good rock breakage.

Written by J. ROTH


Nitrosyl Chloride. NOCl, mw 65.47, N 21.40%; very corrosive, reddish-yellow gas; mp –59.6°, bp –5.38°, decomps by w, sol in fuming sulfuric acid. Critical temp 167°, crit press 92.4 atm (Ref 4)

Can be prep’d from Na nitrite and hydrochloric acid; NaNO₂+2HCl=NOCl+NaCl+H₂O (Ref 1)

NOCl is a powerful oxidizing agent, and causes exxps when mixed with reducing substances. For instance, an exph occurs when it is mixed with an equal quantity of hydrogen. When powdered As or Sb is introduced into gaseous NOCl, spontaneous combustion occurs. An exph reaction was reported when it was sealed in a tube with a residue of acet in the presence of Pt catalyst (Ref 2)


Nitrosyl Fluoride. NOF, mw 49.01, N 28.58%; colorless gas, often bluish because of impurities; mp –132.5°, bp –59.9°; d solid, 1.71g/cc; d liq at –59°, 1.326g/cc. Sol in w with blue color evolving NO, HNO₃ and HF

Can be prep’d by treating nitrosyl chloride with Ag fluoride (Ref 1), or by the combination of nitric oxide and fluoride (Ref 2)

NOF reacts violently with B, Si, red P, Sb and As even under cold conditions, and on heating with some organic comps (Ref 6). It reacts vigorously with glass and corrodes quartz (Ref 8). When mixed, even at low temps, with the relatively inactive OF₂, it explds (Ref 4). It can be kept in quartz ampules if cooled in liq oxygen

NOF is highly irritating to the skin, eyes and mucous membranes (Ref 5)

Refs: 1) O. Ruff & K. Stauber, ZAnorgChem
47, 190 (1905) 2) O. Ruff, W. Menzel & W. Neumann, ZAnorgChem 208, 293 (1932)

Nitrosyl Perchlorate. NOClO₄, mw 129.47, N 10.82%; white cryst, decomps on heating, hygroscopic, d 2.169g/cc, unstable
First prepd by Hofmann and Zedtwitz (Ref 1) by passing a mix of nitric oxide and nitrogen dioxide into 72% perchloric acid. The acid was then evaporated at 100°C, and on cooling the hydrate, NOClO₄·H₂O, crystd out. The product was dehydrated in vacuo over phosphorous pentoxide.

When heated below 100° it decomps (Ref 2) according to the equation:
2NOClO₄ → 2ClO₄⁻ + N₂O₅ + 1/2O₂. At higher temp the compn follows a different course:
2NOClO₄ → Cl₂ + N₂O₅ + 3O₂. It is strongly endothermic with ΔHf = -41.79 ± 0.08 kcal/mole.

It reacts with w. with the evolution of nitrogen oxides. With methanol it forms methyl nitrite, while ethanol, ether or acct react with ignitions and explosns. Violent expls occur with primary aromatic amines, probably because of the formation of diazonium perchlorates (Ref 3).


Nitrosylsulfuric Acid (Nitroso, Nitrosyl Sulfate, Nitrosulfuric Acid, Nitroxyl sulfuric Acid, Nitrosulfonic Acid, Nitrosyl Hydrogen Sulfate, Nitro Acid Sulfite). HNO₃-SO₃, NO₂HSO₃, HNO₃SO₃, ONO₂SO₃H, mw 127.08, N 11.02%, colorl prisms; mp, decomps 73.5°. In moist air the crstls decomps with the formation of sulfuric acid and nitric acids, and above 50°, nitric oxide and nitrogen dioxide are evolved. Decomps violently with w. with formation of sulfuric acid and nitrogen oxides.

HO-S-ONO

O

Sol in sulfuric acid contg not more than 30% w. otherwise it is decomps by the w. in the acid

Formed as an intermediate in the Pb chamber process for sulfuric acid by the reaction of sulfur dioxide, nitrogen trioxide, oxygen and w. (chamber crystals) (Refs 1 & 2). Can be prepd from Ag acid sulfate and nitrosyl bromide (Ref 4).

In the expl industry, it is constantly necessary to deal with nitrosylsulfuric acid, because it forms during the nitration of organic compds as a result of the partial oxidation of the compds by nitric acid. For example, in the manuf of TNT, a small amt forms during the mononitrification:
C₆H₅CH₃+18H₂SO₄+18HNO₃ → 18HNO₃O₄+7CO₂+22H₂O

Larger amts form during dinitration, and still larger amts, reaching 15–18% of the total acidity, during trinitration.

In the nitration of glycerin to NG, the reaction proceeds as follows:
C₃H₅(OH)₃+7H₂SO₄+7HNO₃ → 7HNO₃O₄+3CO₂+11H₂O, and in the nitration of cellulose to NC, or of starch to Nitrostarch:
C₆H₁₀O₅+12H₂SO₄+12HNO₃ → 12HNO₃O₄+6CO₂+17H₂O

Nitrosylsulfuric acid is highly toxic, and a strong irritant to skin and mucous membranes (Refs 10 & 11).


Nitrous Fumes. This term includes any nitrogen oxide fumes produced in the manuf of nitric
acid or in processes in which it is used. The exact compn of the fumes or vapor depends upon such factors as temp, humidity, and the material the acid acts upon

The oxides of nitrogen are somewhat sol in w, reacting with it in the presence of oxygen to form nitric and nitrous acids. This is the action that takes place deep in the respiratory system.
The acids formed are irritants, causing congestion of the throat and bronchi, and edema of the lungs. The acids are neutralized by the alkalies present in the tissues, with the formation of nitrates and nitrates. The latter may cause some arterial dilation, fall in blood press, headache and dizziness, and there may be some formation of methemoglobin. However, the nitrite effect is of secondary importance.

Because of their relatively low solubility in w, the nitrogen oxides are only slightly irritating to the mucous membranes of the upper respiratory tract. Their warning power is therefore low, and dangerous atms of the fumes may be breathed before the individual notices any real discomfort. Higher concns (60 to 150ppm) cause immediate irritation of the nose and throat, with coughing and burning in the throat and chest. These symptoms are often clear up on breathing fresh air, and the individual may feel well for several hours. Some 6 to 24 hours after exposure, he develops a sensation of tightness and burning in the chest, shortness of breath, sleeplessness and restlessness. Dyspnea and air hunger may increase rapidly, with development of cyanosis and loss of consciousness, followed by death.

In cases which recover from the pulmonary edema, there is usually no permanent disability, but pneumonia may develop later. Concns of 100–150ppm are dangerous for short exposures of 30 to 60 minutes. Concns of 200–700ppm may be fatal after even very short exposures.

Continuous exposure to low concns of the fumes, insufficient to cause pulmonary edema, is said to result in chronic irritation of the respiratory tract, with cough, headache, loss of appetite, dyspepsia, corrosion of the teeth and gradual loss of strength.

Exposure to nitrous fumes is always potentially serious, and persons so exposed should be kept under close observation for at least 48 hours (Refs 1, 2, 3, 5 & 6)

Renaud and Gilbert (Ref 4) developed indic-
cator test paper to detect dangerous levels of nitrous fumes in expl plants

NitroxydialkylNitramines. See Hydroxydialkylaminos, Nitrated Derivatives in Vol 7, H239-L

Nitrylchloride (Nitroxy Chloride). NO2Cl, mw 81.47; corrosive, toxic colorl gas; mp –145°; bp –14.3°, decomp above 120°; vap d at 100°, 2.81g/l; liq d at 0°, 1.37g/cc; at 16°, 1.33g/cc

(Ref 11)
The most important processes for the practical production of nitryl chloride are those in which chlorosulfonic acid and practically anhydr nitric acid are used as starting materials:

HSO3Cl+HNO3 → H2SO4+NO2Cl. The chlorosulfonic acid is added dropwise either at RT or with cooling to –10° to 100% nitric acid or to mixts of conc nitric and sulfuric acids. A continuous current of almost pure nitryl chloride gas is evolved (Refs 1, 3, 4, 5, 6, 8 & 9). Further purification can be achieved by the passage of ozonized O2 thru the liquefied gas (Ref 9). Very pure nitryl chloride is obtained on slow vac distn of anhydr nitric acid on to chlorosulfonic acid in an app consisting entirely of glass, followed by fractional distn (Ref 7)
The gas or liq may attack organic matter with expl violence (Ref 11). Instances of violent re-
actions with ammonia, sulfur trioxide, stannic bromide and iodide are documented (Ref 12)

Nitryl chloride was proposed for use as a nitrating agent for paraffin hydrocarbons (Ref 2)


Nitryl Fluoride (Nitroxy1 Fluoride). NO$_2$F, mw 65.01; color, fuming gas; mp -166.0$^\circ$; bp -72.4$^\circ$; d (solid) 1.924g/cc, liq at -72$^\circ$, 1.796g/cc

Originally prep'd by the spontaneous combustion of nitric oxide in an atm of fluorsine; 4NO$+\text{F}_2 \rightarrow N_2 + 2\text{NO}_2$F (Ref 1). More easily prep'd by mixing nitrogen dioxide with fluorine; 2NO$_2$ + F$_2$ $\rightarrow$ 2NO$_2$F (Ref 2)

Nitryl fluoride spontaneously ignites I$_2$, Se, P (red & white), As, Sb, B, Si, Th and Mo. On mild warming attacks Pb, Bi, Cr, Mn, Fe, Ni, W, S and charcoal. On contact, alc is converted to ethyl nitrate and benz to NB. It attacks mucous membranes instantly (Ref 5)


Nitryl Perchlorate (Nitroxy1 Perchlorate). NO$_2$ClO$_4$, mw 145.47, white crysyst; mp, decomp's rapidly at 120$^\circ$; deflagrates on rapid heating.

Can be prep'd by the action of conc nitric acid on perchloric acid; NO$_2$OH$+\text{HClO}_4$ $\rightarrow$ NO$_2$.ClO$_4$$+\text{H}_2$O

Nitryl perchlorate reacts with organic matter with a violence ranging from slight explos to sharp detonations accompanied by fire. Incidents have been reported with acet, benz & eth (Ref 2)


Nitrol. An expl patented by Schweiz of Sprengstoff-Fabrik AG, Dottikon (SwissP 226852), contg m-dinitrobenzene made more sensitive to initiation by the addition of 30% PETN. It was castable because of the low mp, about 80$^\circ$, of m-DNB

Ref: Stettbacher (1948), 72


Nobel, Alfred Bernhard (1833-1896). Swedish inventor and philanthropist who revolutionized the exs industry. Between 1863 and 1865, in spite of an expn which killed his youngest brother and four other persons, he successfully developed a detonator, based on MF, to make possible the industrial use of NG. This was quickly followed by the development of Dynamite (see Vol 5, D1585 ff), in which the admixture of kieselguhr, while reducing the expl force of NG by one-fourth, provided a blasting material which was reasonably safe in manuf and use. From its first patenting in 1867, Dynamite enjoyed a world-wide success, and in 1875 Nobel introduced the still more powerful Blasting Gelatine (see Vol 5, 1599 ff), in which the NG was gelatinized with collodion cotton. Finally, in 1888 he contributed one of the first smokeless powders for military purposes. This was Ballistite (see Vol 2, B8-B9), a mixt of collodion cotton, NG, benz, and (initially) camphor, which was first used by the government of Italy

In spite of many battles over patent rights, these inventions earned Nobel a considerable fortune, which was increased from his large holdings in the Baku (Russia) petroleum industry. He died in 1896 in San Remo, Italy, leaving a vast fortune, a major part of which established the world-famous prizes for chemistry, physics, physiology or medicine, literature of an idealistic tendency, and the promotion of world peace

A detailed listing of Nobel's inventions, arranged chronologically, follows:

1863: An expl prep'd by dissolving NG in ethyl or methyl nitrate, followed by mixing with BiPdr, NC and other materials

1863: Initiation of NG charges by a detonator incorporating gunpowder

1865: Initiation of NG charges with a modern
1866-67: Invention of kieselguhr Dynamite, and application of MF caps for its initiation
1869: Invention of Straight Dynamite (see Vol 5, D1596-R to D1598-R)
1873: Improvement of AN blasting powder, invented in 1867
1875: Invention of Blasting Gelatine and Gelatine-Dynamite
1879: Invention of Extra Dynamite or Ammonia Gelatin Dynamite, a combination of AN and Blasting Gelatine (see Vol 1, A295-R, Vol 5, D1604-L and Vol 6, E500-L). In this expl, the AN was rendered non-hygrosopic (Ref 3, p335)
1879: Expls suitable for mining or military purposes, contg NG, NC and Nitroso sugar, mixed with nitrates, chlorates or perchlorates of alkali or alkaline earth metals
1884: Expls consisting of combustible liqs, such as petroleum, mixed with nitrates or other oxidizing salts. To this could be added various quantities of explosives, such as NG
1885: A liq expl consisting of 1p of goudron (Fr for tar or pitch) dissolved in 2p of NG. This soln was mixed just before use with 2p of oleic acid
1885: Addition to NG of materials having a tendency to lower its fp
1886-87: Expls suitable for charging shells or torpedoes, consisting of compressed gaseous expl mixts with or without liq or solid expls or combustibles
1887: Safety expls contg Cu nitrateammine, Cu(NO3)2-4NH3, either alone or in mixt with combustibles
1887: Improvements in detonator manuf, described in FrP 184129 of 1887 (Ref 1, pp 198–99)
1887: Smokeless powders prepbd by gelatinizing with a vol solvent, NC's prepbd from such materials as corozo, coconut shells, etc, together with Nitrostarch or Nitroderiv
1888: Invention of Ballistite, the first successful smokeless powder contg NG, described in BritP 1471 of 1888 (Ref 1, p 51)
1888: An expl for use in detonators contg 2p colloidion cotton dissolved in 12p acet, to which was added 1p NG, 4p K pichrate and 8p K chloride (Ref 1, p 199)

1888: An expl prepbd by mixing Ba nitrate, charcoal and Amm pichrate or amorph P
1888: An expl consisting of 3p Ba nitrate and 1p AN, together with a small quant of dextrin or gum as binder
1888-89: A cordeau détonant contg Blasting Gelatine with 15-20% camphor, as well as K chloride, K ferrocyanide and NC
1891: A smokeless powder prepbd by carefully blending pulped NC (70 to 99p) with liq nitroaromatic compds (30 to 1p), heating the mass and pressing it in the form of plates, which were cut into sections and granulated in the manner practiced with BkPdr. This was one of the first "solventless" methods of proplnt prepn (Ref 1, p 5)
1894: A cordeau détonant contg a compn prepbd by thoroughly mixing NG or Nitroso sugar with NC, mononitrosaphthalene, dinitrobenzene, di- or trinitrotoluene, K dichromate & K ferricyanide (FrP 237447 of 1894) (Ref 1, pp 158–159)
1894: Smokeless powders prepbd by blending NC and Nitromannite, with or without dinitrobenzene (DNB). No 1: NC 60, Nitromannite 40; No 2: NC 60, Nitromannite 20, DNB 20; No 3: NC 50, Nitromannite 30 & DNB 20% (Ref 1, p 580)
1896: A safety mining expl contg AN as the main ingredient, together with K permanganate and a small quantity (1–3%) of NG (Ref 1, p 5)
1897: A safety mining expl contg K chloride 40, Na bicarbonate 33.3 & dextrin 26.7%
1896-97: A progressive burning smokeless powder, patented by Nobel shortly before his death, consisted of a core of rapid burning powder, such as Ballistite, surrounded by a coating of a slow burning compn

There were many other expl compns patented after Nobel's death by the numerous companies established by him throughout the world. Some are given below:

Nobel Ardeer Powder. A Dynamite manufbd in the early twentieth century by Nobel's Explosive Co, Ardeer, Scotland. It contd NG 31–34, kieselguhr 11–14, Etspom salt 47–51, K nitrate 4–6, soda 0.5 & Amm carbonate 0.5% (Ref 1, p 30)

Nobelit. One of the permissible Gelatine-Dynamites manufbd by the Nobel Explosive Co. It contd NG 28.0, colloidion cotton 0.7, AN 39.7, dextrin 2.5, potato flour 10.0, vegetable oil
0.5, woodmeal 1.0 & Na chloride 17.6%

**Nobel’s Carbonite.** A dynamite manufd at the end of the 19th century in England by Nobel’s Explosives, Ltd. It contd NG 25 to 27, K nitrate 28 to 32, Ba nitrate 3.5 to 4.5, wheat flour or woodmeal 31.2 to 37.8, & moisture 3.9 to 8.4%. To this were added Na bicarbonate or Ca carbonate 0.5 and benz 0.5% (Ref 1, p 114)

**Nobel’s Gelyngite.** A Dynamite manufd in England between 1897 and 1898, contg NG 54 to 63, collodion cotton 3 to 5, K nitrate 26 to 34 & woodmeal 6 to 9% (Ref 1, p 340)


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**Nobel’s Mortar** (Mortero probeta de Nobel in Spanish). A device for testing the strength of expls

**Historical.** Shortly after the invention of gunpowder (BkPDr), it was recognized that a test had to be developed to evaluate its properties. As it was first used only as a proplnt and not as a HE, it was sufficient to test it solely for burning rate. One of the first devices to test the strength of BkPDr was described by Bourne in 1578 (Ref 1). It consisted of a small metal cylinder closed at the top with a heavy lid, one side of which was attached to a hinge, the other side being connected to a ratchet. When a charge of BkPDr was fired inside the cylinder, the resulting pressure raised the lid to a certain angle, and the ratchet prevented it from falling back. The angle was measured and related to the power of the particular batch of BkPDr.

A better instrument was devised in 1627 by Curtenbach. It consisted of a small mortar with a heavy cylindrical shot positioned at its mouth. When a charge was fired, the shot travelled at a 45° angle along a stretched wire, provided with a series of catches to stop the shot at the highest position it attained. This device can be considered to be the prototype of the modern Ballistic Mortar (See Vol 1, VII). The same device was described in 1647 by Nye in his “Art of Gunnery”. However, he advised firing the shot into clay in order to detect the depth to which it was buried. This design was adopted by the French Government in a device called the “Mortar Éprouvette”. The next improvement was that of Robbins, who in 1742 invented the “Ballistic Pendulum” (See Vol 1, VII–VIII), by means of which the actual velocity of a projectile could be measured.

Nobel’s mortar, which can be considered as an improvement over that of Curtenbach, consisted of an iron block provided with a cylindrical cavity, 25cm deep and 10cm in diameter. A 10g sample of expl was weighed into a wooden shell, 6cm deep and 3cm in external diameter, which was then inserted into the cavity. A length of safety fuse with a detonator at its lower end was then inserted in the charge. The shot, consisting of an iron cylinder slightly smaller than 10cm in diameter, which weighed exactly 15kg, was then inserted in the cavity. This cylinder was provided with a channel parallel to its axis, thru which the safety fuse ran to the outside of the app. After the gun was positioned at a 45° angle, the fuse was ignited, and the shot was fired. The distance traveled was then compared to that obtained with 10g of a standard expl (Ref 3).

Barnett (Ref 2) gives the following distances obtained for some Brit expls with Nobel’s mortar: Blasting Gelatine, 240m; Gelyngite, 168m; Gelatine Dynamite, 188m; Dynamite No 1, 132m; and Brit “Permitted” Expls, 80–120m

**Note:** In order to avoid having to recover the shot after each test, the gun was sometimes mounted as a pendulum, and the shot fired into a sand bank a few feet away. In this case, the recoil was measured in a manner similar to that of a Ballistic Pendulum


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**Nobel’s Patent Blasting Oil.** Name under which NG was known in the USA at the time of its introduction in the 1860’s

*Ref:* VanGelder & Schlatter (1927), 324

**Nobel’s Powder-Dynamite** (La Poudre-Dynamite de Nobel in Fr). Smokeless powds similar to Ballistite manufd by the Nobel Co. One compn
was prepd by mixing 4–5p of NC with 20p of NG. To this were added 4p of camphor, 20p of Nitrocelulose (12.5% N), and 40p of Nitroglycerin (12.5% N). The mix was blended at 60°C, passed thru heated rolls several times, and the resulting thin sheets cut to desired dimensions. This propellant, manuf'd at the end of the last century, was an example of early solventless powders. One of the varieties of "Powder-Dynamites" was known in Germany under the name "RGP 88 Pulver", and was used in cannons of various caliber.

Ref: Daniel (1902), 581–2

Nobel's Safety Powder. The name given to Dynamite at the time of its invention.

Ref: Davis (1943), 332

Nobel, Sir Andrew (1832–1915). British artillery officer who did important work in ordnance and expls. He invented a chronoscope in 1862, and modified the press gauges existing at that time, creating a model which, with some modification, is still used. This gauge, patented in 1868, was called a "Crusher Gauge", and was designed to estimate the press developed on an expln. It consisted of a heavy-walled cylinder, closed at one end and fitted at the opposite end with a steel piston. A copper cylinder of known dimensions was placed inside the app behind the piston. The ensemble was then screwed into the wall of a gun barrel, or placed in the breech behind the charge. On firing, the press of the gases developed pushed the piston against the copper cylinder, causing its deformation (compression), the greater the press, the shorter its length. Calibration of the copper cylinder under known press loads allowed for an estimate of the press developed in a gun to be made.


Nobel's 704. See under British Military Explosives and Propellants in Vol 2, B301-R

Nobel's Watte Dynamit I. One of the older permissible Dynamites contg NG 30, Na nitrate 31, flour 30, woodmeal 6, naphthalene 2 & Al 1%.

Refs: 1) Marshall 2 (1917), 492  2) PATR 2510 (1958), Ger 122-R

Nobelit (Nobelite). A type of permissible Gelatine-Dynamites used before and after WWI. Two examples are given in the following table:

**Table 1**

<table>
<thead>
<tr>
<th>Compo (%) and some properties</th>
<th>Nobelite</th>
<th>Nobelite 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG (gelatinized with NC)</td>
<td>28.7</td>
<td>26.0</td>
</tr>
<tr>
<td>DNT</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Dextrin</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Woodmeal</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Potato flour</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Amm nitrate</td>
<td>39.7</td>
<td>34.0</td>
</tr>
<tr>
<td>Amm chloride</td>
<td>17.6</td>
<td>32.0</td>
</tr>
<tr>
<td>Satd soln of Ca nitrate</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Oxygen Balance, %</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Velocity of Detonation, m/sec</td>
<td></td>
<td>3750</td>
</tr>
<tr>
<td>Trauzl test, cc</td>
<td>270</td>
<td>220</td>
</tr>
</tbody>
</table>

Refs: 1) Naoum, Exps (1927), 150  2) Naoum, NG (1928), 407  3) PATR 2510 (1958), Ger 122-R

Nobelita Antigrisú Gelatinizada (Span). See under Spanish Permissible Explosives in Vol 3, C455-L

Nobelité (Fr). A plastic expl manuf'd before and after WWII by the Société Nobel Française. It contgned NG 20, collodion cotton 1.6, AN 60, Liq DNT 14, woodflour 4.3, and Na bicarbonate 0.1%. Its c.u.p. (coefficient d’utilisation pratique) was 78 vs 100 for PA, and it was difficult to detonate.

Refs: 1) Pepin Lehalleur (1935), 342  2) L. Médard, MP 32, 217 (1950)

No-Fire Level. The max level of electric energy input that will in no case, within a specified time, initiate an expl-actuated device.


NOL No 130 Primer Mixture. See under Lead Styphnate, Basic in Vol 5, D1278-L
nombre de Moisson (Fr). See Moisson Number in this Vol

NONA (Nonanitroterphenyl; 2,2',2''4,4',4'', 6,6',6''-Nonanitroterphenyl). C_{18}H_{18}N_{6}O_{18}, mw 635.31, N 18.85%, OB' to CO_{2} - 51.63%, light yell monocl cryst, mp 440-50° decompn, d 1.78g/cc

NONA was prep'd in a mixed Ullman reaction using picryl chloride, 1,3-dichloro-2,4,6-trinitrobenzene and electrolytic Cu dust;

\[
\begin{align*}
\text{NO}_2 \quad \text{Cl} &+ \text{O}_2 \text{N} \text{Cl} + 4\text{Cu} \xrightarrow{\text{C}_6\text{H}_5\text{NO}_2} \text{NO}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{NO}_2 \quad \text{O}_2 \text{N} \quad \text{NO}_2 + 2\text{Cu}_{2}\text{Cl}_2 \\
\end{align*}
\]

Thirty g (0.12 mole) of thoroughly dried picryl chloride was dissolved in 50ml of anhyd nitrobenzene in a 500ml 3-neck round bottom flask fitted with a mechanical stirrer and an air cooled condenser. The soln is heated to reflux on a heating mantle. From a dropping funnel fitted with a mechanical stirrer, a slurry of 5.6g (0.02 mole) of 1,3-dichloro-2,4,6-trinitrobenzene and 13g of electrolytic Cu dust was added dropwise while stirring vigorously during a 15 minute period. Reflux was continued for an additional ten minutes and the soln was filtered while still hot. The inorganic residue on the filter was washed with several small portions of hot nitrobenzene. The filtrate and washings were concd on an oil bath under reduced press to a thick syrup. A vol of 350ml of toluene was added, the mixt was refluxed for 15 minutes and filtered hot. The dark brown residue (ca 8g) was suspended in 350ml of toluene, and the mixt was refluxed again for 15 minutes and filtered while hot. The residue on the filter was a brown powdery solid which weighed 5.5g after drying in air. It was not further investigated. The combined filtrates and washings were filtered thru a 3” pad of silicic acid on a 90mm sintered glass funnel, and the adsorbent pad was washed with toluene until a bright yell band had moved near the bottom of the filter. The filtrate was evapd to dryness, the residue added to 300ml of toluene, and the mixt refluxed for 15 minutes and filtered. The product recovered on the funnel was a tan crystn material which weighed 2.4g after drying. It was purified in two portions by chromatography on silicic acid—Celite 535 with a yield of 2.0g of a light yell crystn solid which melted on a hot bar between 440°-450°.

All analytical and test samples were recrystd from either acet-n-hexane mixes or acetonitrile and dried in an Abderhalden drying app over refluxing nitrobenzene for at least 4 hours. The product was identified as 2,2',2''4,4',4'',6,6',6''-nonanitroterphenyl by elemental analysis and X-ray molecular wt detn. Note: The elemental analyses were difficult to perform due to the tendency of the compd to expd in the combustion tube (Ref 1)

NONA has an impact sensitivity of 39cm vs 32cm for Tetryl and 160cm for TNT. Its vacuum stability at 260° is 0.4cc/g/hr

NONA combines exceptional heat stability with a very low vap press, making it attractive as a booster exp in space applications

Refs: 1) J.C. Dacons, “Heat Resistant Explosives VIII; 2,2',4,4',6,6''Hexanitrobiphenyl (HNB) & 2,2',2''4,4',4'',6,6',6''-Nonanitroterphenyl” (Confid), Navord Rept 6904 (15 June 1960) (declassified 15 June 1972) 2) Anon., “2,2',2'',4,4',4'',6,6',6''-Nonanitroterphenyl (NONA)”, Summary Rept Contr No NOW 60-0745-C, American Cyanamid Co, New Castle, Pa (Oct 1964 to Apr 1965) (Confid—material not used in above article)

Nonaqueous Titration Methods. See under Nitrogen Determination in Energetic Materials in this Vol
Noncased Charges. These are contained in one or more combustible bags instead of a cartridge case. Guns utilizing these charges must provide for obturation against rearward escape of gases by features built into the gun breech. Variations include the following: (1) Complete propellant charge in one bag. This arrangement can be used where the resulting size and shape is suitable for handling and loading. One or more elements of igniter material (usually BkPdr), formed as end pads or as a central core, are fixed within the propellant bag to augment the primer flame in effecting thorough ignition of the entire mass of propellant. The propellant bag (sometimes termed cartridge bag) constitutes one unit of separate loading ammo, in which the projectile, propellant and primer are separately inserted into the gun. (2) Propellant charge in two or more bags: (a) This arrangement is used in separate loading ammo either to divide the propellant into portions more easily handled in gun loading, or to provide a basic charge and increments for zone firing. An ignition charge may be included in the basic charge only, or in the increment charges also, as may be necessary for satisfactory ignition; (b) Separately bagged (or wrapped) basic charge and increments are also utilized as components of semifixed ammo for zone firing of muzzle-loading mortars. In this use the separate portions of the complete charge are attached to the fins or fin shaft of the projectile, with the increments readily removable in the field to reduce the range from the maximum to the zone desired. A primer cartridge is carried in the rear of the fin shaft of the projectile. (3) Grain arrangement. Generally, whether cased or bagged, propellant charges composed of the commonly used shapes of grain are assembled with the grains in random positions. However, where large rod-shaped grains are used in a package of large length-to-diameter ratio, improvement in compactness, rigidity and uniformity can be obtained by orderly arrangement of grains, end to end, with axes parallel to the axis of the container. A charge thus arranged is termed a stacked charge.

Also see Vol 1, A385-L under Semi-fixed Ammunition & Separate-loaded Ammunition, and Vol 2, B167-L under Black Powder or Gunpowder. Combustible and Consumable Cartridge Cases are discussed in Vol 3, C420-R ff

Ref: Anon, "Guns-General", EngDesHdbk AMCP 706-250 (1964), pp 5-5 to 5-6

Nonideal Detonation. See under Detonation, Ideal and Nonideal in Vol 4, D389-R to D390-R

Non-Permissible (Amer) or Non-Permitted (Brit) Explosives. See under Commercial or Industrial Explosives in Vol 3, C435-R to C437-R, and Coal Mining Explosives, Testing for Permissibility in Vol 3, C368-R ff

Nord 5210 (SS.11 and AS.11). A Fr line-of-sight wire-guided battlefield missile that can be fired from aircraft, vehicles and ships. The SS.11 is a surface-to-surface version, and the AS.11 is a similar air-to-surface version.

The operator acquires the target by means of a magnifying optical device. As soon as the missile enters his field of vision after launch, the operator commands it to his line of sight by means of a joy-stick. The signals are transmitted over wires trailed from the missile. Tracer flares are installed on the rear of the missile for visual reference. When installed in a helicopter or ship, the simple sighting device used for land vehicles is replaced by a special stabilized sight.

The missile has an overall length of 120cm, a launching wt of 29.9kg, an average cruising speed of 360–584km/hour, and a range of 500–3000m. It is propelled by a two-stage solid propellant rocket motor.

Since 1962, the SS.11B1 version, using transistorized firing equipment, has been in production. It is available with a variety of different warheads, including an inert type for practice. The Type 140AC anti-tank warhead is capable of perforating 60cm of armor plate, the Type 140AP02 explo warhead (2.6kg of expl) will penetrate a 1 cm thick armored steel plate at a 3000m range and expld about 2.1m behind the point of impact, and the Type 140AP59 high-fragmentation anti-personnel type with contact fuse.

This missile is used by some 18 countries, including the USA where it is designated AGM-22A

Nord SS.12. A spin-stabilized, wire-guided surface-to-surface missile system derived from the Nord SS.11. The principal change is the incorporation of a much larger warhead (29.9kg of HE) which makes it effective against fortifications as well as tanks, ships and other vehicles. Available warheads include the Type OP.3C which can pierce
more than 40mm of armor and expld on the other side

The missile has an overall length of 187cm, a launch wt of 75kg, an avg speed of 190m/sec, and a range of 6000m


Nordenfelt and Meurling Powder. A proplnt patented in Engl in 1884, prepd as follows:
Cotton or other cellulosic material, was transformed into a material resembling hydrocellulose thru treatment with hydrochloric acid. It was then dried, pulverized, and mixed with S disd in carbon disulfide. After evap of the CS₂, the material was treated with a concd soln of K nitrate, granulated and dried
Ref: Daniel (1902), 583

Norrbom, J.H. (1835–1907). A Swedish inventor, who, in collaboration with C.J. Ohlsson, introduced the first AN blasting powder, called Ammoniakkrut (see Vol 1, A306-R to A307-L)

Norris Powder. A low-freezing mining expl invented in 1901 by an American, Norris. It was much less sensitive to impact and friction than contemporary Dynamites. It contained NG 70, mononitrobenzene 15, and "Huile empyromatique" 15%. The latter ingredient consisted of an oily substance obtained on distn of wood tar. This expl could be used for underwater blasting
Ref: Daniel (1902), 586–7

Norsabite. An AN coal mining expl of the Favier type contg a small amt of calcium silicide as sensitizer; AN 68, TNT 12, NaCl 17 & Ca silicide 3%. Power by BalPend is 2.64" vs 3.27" for standard Brit 60% Gelignite
Ref: Marshall 3 (1932), 119

Normal Powder (Normalpulver). A Swedish proplnt invented by E. Schenker and manufd at the turn of the century by the Aktiebolaget Svenska Krutfaktorerna at Landskrona and at Amnestoff. The formulation for use in the Swedish Army rifle contained Guncotton 96.2, sol cotton 1.8, resin, a stabilizer and other materials 2.0%. These proplnts were very stable, nearly hygroscopic, and produced much lower temps than corresponding double-base powders such as Cordite, Ballistite, etc. As a result, gun barrel life was lengthened

Normal Powders were also subsequently manufd in Switzerland, Denmark, England, Belgium and Australia

These proplnts gave very satisfactory performance. They developed a muzzle velocity of 1640 ft/sec and a press of 1750 atm, when used in 84cm field guns with a 600g charge and a 6.7kg projectile. In the 7.5mm rifle, with a 2g charge and a 13.8g bullet, a muzzle velocity of 2035 ft/sec and a press of 2200 atm were attained
Ref: 1) P.G. Sanford, "Nitroexplosives", London (1896), 186–7
2) Daniel (1902), 584
3) Brunswig, Props (1926), 134
4) Thorpe 4 (1940), 515

Nougat Method. A method of charging large caliber shells and mines by making successive layers of rough fragments of expl, which are cemented in place by liq expl. A layer of fragments from 1" to 2" thick is placed on the bottom of a container and molten expl run in until the fragments are just submerged. When this layer has solidified the process is repeated until the container is full. By employing this method contraction cavities do not occur, but it is naturally a comparatively slow process

In the case of small caliber shells, etc., it is usually possible to fill them completely with fragments, heat the whole until its temp exceeds the mp of the fusible ingredient, which is then added, and the whole allowed to cool

The process provides a useful means of making a composite expl in that the fragments may be a totally different compd from that used to cement them together. Such a process can be used as a means of prepg an expl contg a high percentage of insuboble constituents which may either be nitro-comps or oxidizers
Ref: 1) Chemische Fabrik Griesheim, GerP 69897 (1892) (TNT–Picric Acid composite)
2) Colver (1938), 320, 458, 697
Novit (Swed). An underwater expl consisting of TNT 50% and Hexanitrodiphenylamine (HNDPhA) 50%, invented prior to WWI. Its properties were: loading d, 1.65–1.68g/cc; relative brisance, 103% (TNT 100%); Qe 1060cal/g (TNT 950); power by Trauzl Pb block test, 315cc (TNT 290cc); and vel of deton 17200m/sec (TNT 6800).

A similar mixt was used in Ger during WWI for loading torpedoes and mines (the name used for HNDPhA was Hexyl).

At the time of WWI some pulverized Al was incorporated in the Novit formulation and this considerably increased its efficiency, especially for underwater applications. A similar expl contg TNT 55.7, HNDPhA 27.9 & Al 16.4%, was used in Ger for torpedoes and mines. The Japanese used a comp similar to Novit under the names “Seigata” and “Type 97 Explosive.”

Refs: 1) Stetthacher (1933), 294 (listed in the index under Torpedomenfüllmittel) 2) A. Stetthacher, Protar 9 (1943), 38 & 41 3) Bebie (1943), 112 4) Anon, “Allied & Enemy Explosives”, Aberdeen Proving Ground, Md (1946), 107

Novo-Astralit (New Astralite). Russ pre-WWI mining expl contg AN 80.8, TNT 16.0, potato meal 3.0 & sawdust 0.2%
Ref: Anon, SS 12, 428 (1917)

Novo-Nobelits (New Nobelites). Russ pre-WWI coal mining expls contg NG (gelatinized with collodion cotton) 11.5–12, AN 47–50, Na nitrate 4–3, glycerin 3.5–4, potato meal 6, Na chloride 22–20, & talcum 6%
Ref: Anon, SS 12, 410 (1917)

NOX. Code name for 1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane

Nozzle Theory of Detonation. See Detonation (and Explosion), Nozzle Theory or Expanding Jet Theory of Jones in Vol 4, D460-R

NPMn 95/5 (Fr). A booster expl mixt of 95/5 PETN/mononitronaphthalene, compressed to a d of 1.6g/cc, was used to determine the vel of deton of ethylenediaminedinitrate (Ref 1). It was called Mélange NPMn 95/5 by L. Médard (Ref 2) who used it at a d of 1.6g/cc in 30mm cartridges having charge wts of from 10 to 50g. He claimed that it possessed the same initiating efficiency as straight PETN, but was easier to compress and did not break on handling. Médard also recommended its use as a booster expl in lieu of PA or Tetryl (Ref 3)

Refs: 1) A. LeRoux, MP 32, 123 (1950) 2) L. Médard, MP 33, 339 (1951) 3) Ibid, MP 34, 102 (footnote) (1952)

NS (Nitrate of Soda). Brit for Na nitrate

NS (Nitrate of Soda) Gelignites. Brit NG expls of the Gelignite type contg Na nitrate which were cheaper than those contg K nitrate. See under Gelignite in Vol 6, G57-R to G58-R
Ref: Taylor & Gay (1958), 25

NSDI and NSDII. Span solventless (sin dissolvente) double-base propints intended for use in large cal guns
Ref: Vivas, Feigenspan & Ladrega 3 (1948), 405

NSX. Designation for Nitrostarch Demolition Explosive. See under Nitrostarch in this Vol

NT (Explosif) (Nitrate d'ammoniaque-Tolite). A Fr military expl consisting of AN 70 & TNT 30%. This castable compn corresponds to the US 70/30 Amatol

NTMX (Explosif) (Nitrate d'ammoniaque-Tritritrometaxylene). A Fr military expl consisting of AN 78 & Trinitroxylene 22%, used as a bursting charge in projectiles
Ref: Anon, “Handbook of Foreign Explosives”, FSTC 381-5042, US Army Foreign Science and Technology Center (Oct 1965), 131 & 229
NTN. A liq expl consisting of a mixt of Nitromethane 51.7, Tetranitromethane 33.2, and 1-Nitropropane 15.1% by wt. A clear, light yel homogeneous liq between -58° and 100°; d 1.269-0.0014T (T in °C)/cc. Impact sensitivity (50% height, NOL 2.5kg wt), 31.4cm vs 320cm for TNT. It is insensitive to electric sparks, non-reactive in air, and insol in w. Its sensitivity and stability meet military requirements


NUCLEAR ACTIVATION.
ANALYSIS AND DETECTION

Nuclear activation analysis (NAA) is a method for qualitatively and quantitatively detg elemental compn by means of nuclear transmutations. The method involves the irradiation or bombardment of samples with nuclear particles or high-energy electromagnetic radiation for the specific purpose of creating radioactive isotopes from the stable or naturally-occurring elements present. From the numbers, types and quantities of radioactive elements or radionuclides, it is possible to deduce information about the elemental compn of the original sample.

NAA has been most frequently associated with the nuclear reactor as a tool because of the availability of intense beams of neutrons at thermal energies (0.025eV) from such facilities. Many elements have a reasonably large probability (cross-section) for thermal neutron capture. This can result in a radioactive product from the $A(n, \gamma A')$ reaction where $A$ is the stable element, $n$ is a thermal neutron, $A'$ is the radioactive product of one atomic mass unit greater than $A$, and $\gamma$ is the prompt gamma ray resulting from the reaction. $A'$ is usually a beta and/or gamma emitter of reasonably long half-life. Where access to a nuclear reactor has been convenient, thermal neutron activation analysis has proven to be an extremely valuable nondestructive analytical tool and in many cases, the only method for performing specific analyses at high sensitivities.

NAA based upon fast neutron-induced reactions has also been extensively utilized. This technique is applied to systems which produce radionuclides by the general reaction $A(n, q)B$.

where $A$ is again the stable element, $n$ is a fast or high-energy neutron, $q$ is a nuclear particle (not a $\gamma$-ray), and $B$ is the radioactive product, usually (but not always) of an atomic mass different from $A$. Thus, such reactions as $(n, p)$, $(n, 2n)$, $(n, \alpha)$, $(n, n')$, $(n, d)$, and $(n, t)$ are included in this category. The thresholds for these particle-particle reactions, i.e., the energies required to induce the reactions, with few exceptions, are in the 1 MeV and higher regions.

The greatest amt of work with fast neutrons has been in the 14 MeV range. This has resulted from the commercial development of small, low cost particle accelerators, called neutron generators, utilizing the $t(d, n)x$ reaction. In these devices, deuterium ($d$) ions are accelerated into metal targets sdd with tritium (t) gas. The result is a beam of neutrons with an average energy of 14.7 MeV, and $\alpha$ particles (He ions) as a product. Activation products formed from these high energy neutrons are usually produced in much lower yields and possess much shorter half-lives than those from the $(n, \gamma)$ thermal neutron reaction. However, using such neutrons in combination with rapid transfer sample systems and gamma-ray spectrometry, elemental analysis on a wide range of elements, in particular the lighter ones, can be performed on a routine basis.

An additional source of neutrons for NAA, other than reactors or accelerators, are radioactive isotopes, which either in combination with other stable elements or by their own decay, emit neutrons. The advantage and attraction of these encapsulated sources are their small size and wt, and complete absence of operational or maintenance problems. The most widely utilized of such sources is californium-252 ($^{252}\text{ Cf}$) which decays by spontaneous fission and emits neutrons in copious amts per unit wt. $^{252}\text{ Cf}$ is made by bombarding plutonium-239 ($^{239}\text{ Pu}$) in a very high intensity nuclear reactor. Elements of higher atomic number are built up by successive neutron captures. Thirteen successive neutrons must be added to each nucleus of $^{239}\text{ Pu}$ to convert it to $^{252}\text{ Cf}$. The important nuclear properties of this new man-made element are:

- **Effective half-life**: 2.65 yrs
- **Average neutron energy**: 2.35 MeV
- **Neutron emission rate**: $3.4 \times 10^{12}$ neutrons/sec/gram
- **Decay heat**: 38.5 watts/gram
Individual sources of $^{252}$Cf are currently available in quantities up to 10–50 mgs of the element. Such sources, when contained in a suitable hydrogenous moderator, can provide thermal neutron outputs adequate for the activation analysis of many elements in the fraction of a percent wt range.

The measurement of the prompt gamma ray following neutron capture in the $(n, \gamma)$ reaction with thermal neutrons is an alternate method of NAA and is extensively used. In this method the gamma-ray intensity is dependent only on the neutron capture cross-section and not upon the half-life of the product nucleus. The gammarays to be detected are termed prompt in that they are emitted within $10^{-15}$ sec of the time of neutron capture; thus prompt NAA is generally more difficult to perform because the $\gamma$-ray detector must also be shielded from the source of neutrons. Prompt NAA is particularly useful in process control and measurement applications with flowing or continuous streams of material, or for high volume inspection where nondestructiveness and speed of analysis are important factors.

Other types of NAA involve activation with charged particles and with high energy photons ($\gamma$-rays). However, as of this writing, these have had no applications to energetic materials and are merely mentioned here.


The remainder of this article will be devoted to specific applications of NAA to energetic materials and processes. Areas of interest will include: 1) Elemental Analysis, 2) Determination of Pellet Weight in Primers, 3) Determination of Gunpowder Residues in Forensic Investigations, 4) Detection of Explosives in Buried Mines, 5) Detection of Hidden Explosives in Baggage, and 6) Explosives Safety in Neutron Activation Analysis.

**FIG. 1 NEUTRON GENERATOR FACILITY**

A. SCALING TUBE NEUTRON GENERATOR  
B. 140 KV POWER SUPPLY  
C. CLOSED-LOOP REFRIGERATION SYSTEM  
D. DUAL-AXIS SAMPLE ROTATOR ASSEMBLY  
E. PROTON REACTOR NEUTRON FLUX MONITOR  
F. SAMPLE LOAD STATION AND DUAL CRYSTAL COUNTING ASSEMBLY  
G. CONTROL CONSOLE FOR NEUTRON GENERATOR  
H. PROGRAMMED TIMER FOR SAMPLE TRANSFER SYSTEM  
I. POLYETHYLENE SAMPLE TRANSFER TUBING
The concrete block walls of the cell housing the generator tube and associated components are 1.7 meters thick. The facility also includes a Kaman Nuclear dual-axis rotator assembly for simultaneous transfer and irradiation of reference and unknown sample, and a dual Na iodide (NaI) scintillation detector system designed for simultaneous counting of activated samples. Automatic transfer of samples between load station to the rotator assembly in front of the target, and back to the count station, is accomplished pneumatically by means of two 1.2cm (i.d.) polyethylene tubes which loop down at both ends of the system and pass underneath the concrete shielding thru a pipe duct. Total one-way traverse distance for the samples is approx 9 meters. In performing quantitative analysis for a particular element by neutron activation, the usual approach is to compare the count rates of an unknown sample with that of a reference standard of known compn irradiated under identical conditions.

Based on extensive work on FNAA as applied to gross elemental analysis in the percent range, the conditions for optimum precision and accuracy are as follows: (a) Reference standard and sample to be analyzed should be as similar as possible in compn to minimize interferences from activation of other elements; (b) Reference standard and sample should be as similar as possible with respect to wt, volume and density to minimize geometry counting errors and to eliminate the need for gamma and neutron self-shielding corrections; (c) Simultaneous irradiation of both reference and sample to eliminate neutron flux correction; and (d) Dual-axis rotation of reference and sample during irradiation to insure a uniform neutron dose to both.

Using the above conditions, some representative results are given in Table 1 for total nitrogen content assay of “pure” homogeneous high energy compds by FNAA.

Table 1: Total Nitrogen Content in "Pure" Explosives by High Precision FNAA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Analysis</th>
<th>FNAA a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
<td>12.60</td>
<td>12.57 ± 0.05</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>12.18</td>
<td>12.12 ± 0.10</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>13.11</td>
<td>13.03 ± 0.07</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>13.23</td>
<td>13.23 ± 0.06</td>
</tr>
<tr>
<td>TNT</td>
<td>18.50 a</td>
<td>18.50 ± 0.06</td>
</tr>
<tr>
<td>HMX</td>
<td>37.84 a</td>
<td>37.78 ± 0.06</td>
</tr>
</tbody>
</table>

a theoretical value for pure compound
b values listed are the mean of at least four determinations ± 1σ (std. dev. from the mean)

TNT and HMX were from highly purified laboratory samples and the nitrogen contents listed are calcd values for the pure compds. Precision and accuracy as indicated by the FNAA data for these compds are excellent and most likely represent the optimum that can be achieved by this technique.

For the analyses given in Table 1, samples were contained in special polyethylene vials specifically designed to fit the Kaman Nuclear dual-axis rotator assembly. These vials are 4.5cm long and 1.0cm o.d. with an internal volume of 2.3cu cm. When filled, a vial contains approx 0.5g of NC and 2.3g of TNT or HMX. A 12.60% NC was used as the reference standard for all samples of this material; TNT and HMX were compared against “pure” samples of each other, respectively.

NC samples were irradiated for 3 min and TNT and HMX for 1 min at a 14 MeV neutron flux of approx 10^6n/cm² sec. Simultaneous counting was performed by means of a matched dual 7.6x7.6cm flat NaI crystal detector assembly in conjunction with a Kaman Nuclear programmed timer system for automatic sample transfer. A one-min count time was usually sufficient to exceed 10^4 counts. The signal from each de-
tector was fed to an individual single-channel pulse height analyzer and only the 0.511 MeV photopeak was counted using a 20% window.

Neutron activation is also used routinely for the assay of binary mixts contg two compds of different nitrogen content. This method has been applied extensively to Octol compns which contain varying proportions of TNT and HMX. The mixture is normally manufd by dispersing finely-divided crystalline HMX in hot molten TNT and cast loading the melt into ammo items. The finished product is designed to contain a specific HMX content in the 60–80% by wt range. Because HMX is not soluble in the molten TNT, non-uniformity of compn can result and hence the need for quality control by chem analysis.

The conventional assay technique is an extraction procedure whereby a 5g sample of Octol is treated with hot benz to remove the TNT and the insoluble HMX is determined gravimetrically. Analysis time per sample is approx 3 hrs and each sample is assayed in duplicate. For this particular product, in addition to a decrease in analysis time, a non-destructive method is especially desirable because of other physical tests that are also required on each sample.

By FNAA, the total nitrogen content of a sample is first detd and then related to compn of the mixture. Since Octols contain no ingredients other than “pure” TNT (18.50% N) and “pure” HMX (37.84%), the following linear relationship is derived from the calcd nitrogen content of each ingredient:

\[
\%\text{HMX} = 5.171 \cdot N - 95.66
\]

where N is the nitrogen content of the mixt in % by wt.

For Octol containing 60–80% HMX, a 0.2% change in nitrogen content is equivalent to approx a 1% change in HMX content. Determination of HMX content, by a non-destructive method, to an accuracy of ± 1% or better, is considered adequate for plant-grade material. At PicArsn (Ref 13), various FNAA techniques were examined with regard to accuracy and precision for the assay of Octol samples. These included: (a) Dual-axis rotation of sample and standard during irradiation followed by sequential counting, ie, counting sample and standard in succession and correcting for decay; (b) Dual-axis rotation of sample and standard with simultaneous counting of both; and (c) Single-axis rotation of standard and one or more unknown samples with sequential counting.

For single-axis rotation, a special lucite wheel is used designed to hold up to 12 small polyethylene vials contg expl. The wheel is manually mounted in front of the accelerator target before irradiation, and manually removed after irradiation for counting the samples.

In Table 2, results are given comparing the three above FNAA techniques for total nitrogen and corresponding HMX content of three synthetic Octol samples containing 70, 60 and 80% HMX respectively. Chemical analysis by extraction is also included as another basis for comparison. An 80/20 Octol (80% HMX) was used as the reference standard for the activation assays.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrogen, %</td>
</tr>
<tr>
<td></td>
<td>Dual-axis rotation, sequential counting</td>
</tr>
<tr>
<td>Sample, %</td>
<td></td>
</tr>
<tr>
<td>70/30</td>
<td>32.03</td>
</tr>
<tr>
<td>60/40</td>
<td>30.11</td>
</tr>
<tr>
<td>80/20</td>
<td>33.98</td>
</tr>
</tbody>
</table>

a Mean of six determinations of each sample ± 1σ (standard deviation from the mean); Value in parenthesis is corresponding %HMX ± 1σ

b Two determinations on each sample, mean given in parenthesis
Analysis by dual-axis rotation yields the best results; agreement with calc'd values for total nitrogen is 0.1% or less in all cases. The corresponding average absolute errors in HMX content for the three samples are 0.45 and 0.26%, respectively, for sequential and simultaneous counting as compared to 0.31% for chem analysis. Differences between the two modes of counting for dual-axis rotation are not considered significant and the choice of counting arrangement is arbitrary for $^{15}$N radioassay in these samples.

Predictably, analysis by single-axis rotation is not comparable in accuracy to dual-axis rotation. The mean absolute error was 0.24 and 1.24% for the total nitrogen and HMX content, respectively. Dual-axis rotation by means of the Kaman assembly, however, despite its undeniably greater accuracy and precision, is limited to only one sample and reference standard per irradiation. It is the preferred method where speed is not essential—but when the number of samples to be analyzed is large, multiple sample irradiation on the lucite wheel with single-axis rotation is used. The precision of this latter technique for six plant samples of Octol is shown in Table 2a. In this series each irradiation consisted of six Octol samples, an 80/20 Octol reference standard and a blank vial mounted on the lucite wheel. The FNAA results are again compared with chem analysis for HMX content. The mean 1σ precision for 10 determinations on each of the six samples is ±1.30% HMX and the average difference between FNAA and chem analysis is 1.05% HMX:

<table>
<thead>
<tr>
<th>Sample</th>
<th>FNAA$^a$</th>
<th>Chemical analysis$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N, %</td>
<td>HMX, %</td>
</tr>
<tr>
<td>1</td>
<td>30.11 ± 0.29</td>
<td>60.02 ± 1.42</td>
</tr>
<tr>
<td>2</td>
<td>30.60 ± 0.22</td>
<td>62.56 ± 1.15</td>
</tr>
<tr>
<td>3</td>
<td>31.94 ± 0.33</td>
<td>70.02 ± 0.94</td>
</tr>
<tr>
<td>4</td>
<td>31.97 ± 0.44</td>
<td>70.16 ± 1.87</td>
</tr>
<tr>
<td>5</td>
<td>32.23 ± 0.25</td>
<td>71.00 ± 1.27</td>
</tr>
<tr>
<td>6</td>
<td>32.29 ± 0.22</td>
<td>71.28 ± 1.14</td>
</tr>
</tbody>
</table>

$^a$ Mean of 10 determinations on each sample ±1σ (standard deviation from the mean)

$^b$ Two determinations on each sample, mean given in parenthesis

In the most recent work at PicArsn on total nitrogen content assay by FNAA, a special triple-axis rotator assembly was designed and fabricated to achieve both high precision and the capability for simultaneous irradiation of multi-samples (Ref 22). The overall diameter is 15cm and the device contains eight sample cavities designed for snap-cap polyethylene vials, 2.3cm long by 0.9cm o.d. The entire rotator is made of Delrin thermoplastic and polyethylene. Seven samples and a standard are rotated around the target of the neutron generator, their own axes, as well as traversing the neutron beam (Fig 2).

The samples rotate around the target at 100rpm by means of an external motor and pulley assembly, and traverse the neutron beam from 1 to 11cm from the target.

Nitrogen analyses with this special rotator assembly are given in Table 3 for apparently "pure" samples of Ammonium Nitrate (AN), TNT and a 70/30 Octol (HMX/TNT) compn.
Fig 2. Triple-Axis Rotator for Fast Neutron Activation of Explosives

Table 3

Fast Neutron Activation Analysis for Nitrogen in Explosives by Triple-Axis Rotation

<table>
<thead>
<tr>
<th>Sample</th>
<th>%N Calculated</th>
<th>%N, determined at different positions&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>34.98</td>
<td>34.95 ± 0.09</td>
</tr>
<tr>
<td>TNT</td>
<td>18.50</td>
<td>18.56 ± 0.07</td>
</tr>
<tr>
<td>Octol 70/30</td>
<td>32.03</td>
<td>32.04 ± 0.09</td>
</tr>
</tbody>
</table>

<sup>a</sup> Mean of six determinations at each position ±1σ
To establish the equivalence of all eight sample positions with regard to neutron dose, a sample of each material was irradiated simultaneously at four different alternative positions along with a reference standard of the same compn. Each of the three expls was assayed six times at each designated position; the mean and standard deviation is given for each set of six determinations.

The results in Table 3 demonstrate that the triple-axis multi-sample rotator will give a precision equal to that of a two-sample dual-axis rotator (as presented in Table 1) with the advantage that seven samples and a ref standard can be irradiated simultaneously and counted sequentially. This system is useful when many research or production samples of organic expls need be analyzed for purity. The 10 min half-life of $^{13}$N is sufficiently long for all eight sample vials to be manually transferred from the irradiation room to the nuclear counting system and sequentially radioassayed at one-min count times.

**Aluminum and Chlorine in Composite Propellants**

At the White Sands Missile Range, NAA has been developed as a non-destructive method for determination of Al and/or chlorine in solid composite propints for quality control purposes (Ref 21). The compn of the propints of interest contain approx 70% Ammonium Perchlorate (AP), 15% Al, 15% binder, and other minor additives. X-ray fluorescence methods had previously been developed for this assay but these were sensitive to matrix effects and particle size.

For the analysis of aluminum, the $^{27}$Al($n,\gamma$)$^{28}$Mg reaction with 141 MeV neutrons, and for chlorine, the $^{37}$Cl($n,\gamma$)$^{38}$Cl reaction with thermal neutrons, gave the best results. It was found possible to produce a useful mix of 14 MeV and thermal neutrons, so that both Al and Cl could be determined simultaneously from a single irradiation. This was accomplished using a Texas-Nuclear Model 9505 150-kv neutron generator which had a max output of approx $10^{11}$ neutrons/sec, and which gave a 14 MeV flux as high as $10^{9}$ neutrons/cm²-sec at 3 cm from the target. For this work, samples were irradiated inside a 30 cm cubic polyethylene box, with a 15 cm cubic cavity and 7.5 cm wall thickness. The samples were about 10 cm from the target and were subjected to fluxes of approx $10^{8}$ neutrons/cm²-sec for 14 MeV neutrons, and $10^{7}$ neutrons/cm²-sec for thermal neutrons. The polyethylene box served to moderate a portion of the fast neutrons down to slow or thermal levels.

Al was determined by counting the $^{27}$Mg activation product, with a half-life of 9.5 min, and its two emitted $\gamma$-rays of 0.842 and 1.013 MeV energies. Cl was assayed by counting $^{38}$Cl, 37.3 min half-life, and $\gamma$-rays of 1.60 and 2.17 MeV. Specific conditions and a discussion of interfering reactions can be found in the original ref. Determination of each element by this NAA method was judged to be sufficiently accurate for quality control purposes with a precision of better than $\pm$ 1%.

**Phosphorus in Composite Propellants**

Rison et al (Ref 4) of the Naval Ordnance Station at Indian Head, Md have described a rapid sensitive method to determine small amts of P in a composite propint using FNAA. In this case, the propint consisted of 60% AP, 20% Al and 20% binder. The small amts of P to be determined were known to be in the binder phase and existed at concns in the propint in the order of 0.05% by wt.

A Kaman Nuclear, Model 1001, 200-kv Neutron Generator was the source of fast neutrons. The $^{31}$P($n,\alpha$)$^{28}$Al reaction gave the best sensitivity for P with a product half-life of 2.3 min and a $\gamma$-photopeak of 1.78 MeV. The only serious interference is from the Al in the matrix which yields the same activation product from the reaction $^{27}$Al($n,\gamma$)$^{28}$Al. This interference can be eliminated in two ways, (a) by chem separation of the P from the Al by extracting the propint with pentane, and (b) thru spectrum stripping by first subtracting the counts due to Al using a different nuclear reaction $^{27}$Al($n,p$)$^{28}$Mg. In this latter case, $^{27}$Mg has a half-life of 9.5 min with a main $\gamma$ energy peak of 0.64 MeV. For a given neutron flux, the ratio of $^{27}$Mg/$^{28}$Al is constant. When the amt of Al present has been determined by counting $^{27}$Mg, the amt of $^{28}$Al can be calcd by dividing the $^{27}$Mg activity by the ratio $^{27}$Mg/$^{28}$Al.

Usually, 1 g of propint is irradiated for 0.5 to 2 min depending on the flux level. Decay time is 45 sec. Counting time is 5 min for $^{28}$Al under the 1.78 MeV peak. Because of its higher initial activity, $^{27}$Mg (from Al activation) is counted 20–40 min after irradiation. The authors estimate an overall relative error of 5% for the
determination of P after chem separation, and a relative error of 15% after spectrum stripping

**Sodium and Potassium in Solid Propellants**

U.S. Navy researchers (Ref 11), using the water-pool nuclear reactor of the Naval Research Laboratory, developed a technique employing NAA and γ-ray spectrometry to determine trace amounts of Na and K in solid rocket propellants. It is believed that traces of alkali metals such as Na and K, when contained in such propellants, cause the concn of free electrons in rocket motor exhaust plumes to increase considerably. The high concn of free electrons, in turn, results in attenuation and modulation of guidance and telemetry signals. Therefore, an accurate and precise technique is required to control the concn of Na and K during rocket propellant manufacture. NAA was selected because of its excellent sensitivity, precision, reasonable accuracy and non-destructiveness. The particular solid propellant matrix studied in this work was composed of ingredients containing the elements H, O, N, Cl and Al.

This NAA technique is based on the nuclear reactions \( ^{23}\text{Na}(n,\gamma)^{24}\text{Na} \) and \( ^{41}\text{K}(n,\gamma)^{42}\text{K} \). Half-lives of the activated products are 15.0 hrs and 12.4 hrs, respectively. For Na analysis, the samples were irradiated in a specially designed thermal column to suppress the fast neutron reaction of \( ^{27}\text{Al}(n,\gamma)^{28}\text{Na} \) which interferes with the reaction for Na. For K analysis, the propellant samples were irradiated at a standard irradiation position of the reactor. For the Na irradiations, the neutron flux in the thermal column was in the order of 10\(^{10} \) neutrons/cm\(^2\)-sec. For the K assays it was approx 10\(^{12} \) neutrons/cm\(^2\)-sec.

A typical procedure for Na assay is: One gram propellant samples sealed in polyethylene vials are irradiated for at least seven hrs in the thermal column. In order to minimize any thermal neutron flux gradient, the samples are rotated uniaxially at 60 rpm. Following irradiation, the samples are allowed to decay for approx 15 hrs to permit all short-lived radioisotopes to decay to insignificance. The 1.369 MeV γ-photopeak of each sample is then counted for 10 min with a 7.6cm x 7.6cm Na iodide scintillation detector coupled to a 400-channel pulse-height analyzer.

For K assays, one gram samples are irradiated in one of the standard irradiation positions for four to five hrs and rotated uniaxially at 20 rpm.

Following a decay period of at least 15 hrs, the 1.524 MeV γ-photopeak of \(^{42}\text{K} \) is counted for 40 min with a Ge-Li solid state detector and a 4096-channel analyzer. This more sophisticated counting system is necessary to obtain the required resolution, since with a Na iodide detector, the 1.524 MeV peak of \(^{42}\text{K} \) overlaps with the 1.369 MeV γ-photopeak of the \(^{24}\text{Na} \) decay spectrum.

The actual amount of Na and K in solid propellant samples is calcd by comparing the sample activity with the activity of a ref sample with known concns of Na and K. In this case, the ref standards consisted of water samples doped with known amounts of Na and K, with all other conditions being the same as for the propellant samples.

With the above NAA techniques, composite solid rocket propellants containing approx 20% Al were analyzed for Na and K at levels as low as 1 ppm at a 95% confidence level (2σ) of approx ± 12% for Na and ± 20% for K.

**Aluminum, Chlorine and Manganese in Energetic Materials**

At PicArsn, both thermal and fast NAA were compared for non-destructive gross element assay in selected materials used in ammo (Ref 14), specifically Al in aluminized high expls (eg Minols), Cl in AP and Mn in manganese dioxide (as used in pyrotechnic flare compns). The nuclear data and reactions for the elements investigated are listed in Table 4:
Table 4
Nuclear Data for Elements Analyzed by Neutron Activation

<table>
<thead>
<tr>
<th>Neutron Energy</th>
<th>Reaction</th>
<th>Cross Section</th>
<th>Half-life</th>
<th>E, MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al  Thermal</td>
<td>$^{27}$Al(n,γ)$^{28}$Al</td>
<td>215</td>
<td>2.3 min</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>$^{27}$Al(n,γ)$^{27}$Mg</td>
<td>80</td>
<td>9.5 min</td>
<td>0.84, 1.02</td>
</tr>
<tr>
<td>Cl  Thermal</td>
<td>$^{37}$Cl(n,γ)$^{38}$Cl</td>
<td>560</td>
<td>37 min</td>
<td>1.60, 2.17</td>
</tr>
<tr>
<td></td>
<td>$^{37}$Cl(n,γ)$^{37}$S</td>
<td>30</td>
<td>5.1 min</td>
<td>3.09</td>
</tr>
<tr>
<td>Mn  Thermal</td>
<td>$^{55}$Mn(n,γ)$^{56}$Mn</td>
<td>13,000</td>
<td>2.6 hr</td>
<td>0.85, 1.81, 2.11</td>
</tr>
<tr>
<td></td>
<td>$^{55}$Mn(n,α)$^{52}$V</td>
<td>50</td>
<td>3.8 min</td>
<td>1.43</td>
</tr>
</tbody>
</table>

For the thermal neutron activations, a 10mg Californium-252 ($^{252}$Cf) source was utilized in a special assembly constructed from a “Neutron Howitzer” (Trademark of Reactor Experiments, Inc). The assembly is a 6-cu ft cylindrical Lucite tank filled with distilled water and containing three access ports (Fig 3). The large spherical container on the right is the shielded storage cask for the $^{252}$Cf neutron source when not in use.

![Image of Picatinny Arsenal Thermal Neutron Activation Analysis Facility](image)

Fig 3 - Picatinny Arsenal Thermal Neutron Activation Analysis Facility

Polyethylene vials containing samples up to 10g are placed in a removable hollow polyethylene sample chamber, which is attached to the end of a solid Lucite rod. The rod is inserted into the vertical port of the tank (moderator), and is rotated by a motor mounted on top to provide a uniform neutron dose on the sample(s). The $^{252}$Cf source is remotely inserted into the moderator thru one of the horizontal ports which contains a polyethylene sleeve as a guide. With this arrangement, the $^{252}$Cf source and sample are 2.5 cm apart, and the measured thermal neutron flux on the sample is approx $1 \times 10^8$ neutrons/cm²·sec. The other horizontal port is available for other activation or beam expts.

For fast neutron activations, the samples were irradiated with a Kaman nuclear neutron generator (Model A711) under conditions similar to those described in this article under the section on total nitrogen content analysis. The samples were rotated on dual-axes during irradiation.

For both methods, the counting rate of an unknown was compared with that of a simultaneously irradiated known sample to eliminate correcting for neutron and gamma self-shielding. A 7.6cm x 7.6cm Na iodide scintillation well detector was used for integral counting of all gamma rays from each sample; a low-energy threshold was selected just below the photopeak of the lowest energy gamma ray. Accuracy and precision of analysis for each element (Table 5) are about equal for both types of activation, and the results, in general, are comparable to what can be expected from wet chem or other destructive instrumental assay methods. For the expts summarized in Table 5, Al and Mn were analyzed in Al₂O₃ and MnSO₄, respectively, as inert simulants for expts containing these elements:
Table 5
Accuracy, Precision and Conditions for Thermal and Fast NAA for Al, Cl and Mn

| Element | Matrix & Matrix & Calculated | Thermal* | Fast** |
|---------|-----------------|---------|
| Al      | Al₂O₃           | 52.91   | 52.10 ±0.33 ±0.33 | 52.58 ±0.30 ±0.30 |
| Cl      | NH₄ClO₂         | 30.17   | 30.33 ±0.13 ±0.13 | 30.12 ±0.30 ±0.30 |
| Mn      | MnSO₄           | 32.51   | 32.65 ±0.37 ±0.37 | 32.70 ±0.41 ±0.41 |

* ~1.5 g of sample of each material
" Mean of 15 or more replicate runs ±1 0; 1-min count
© ~10 mg ³¹Cl source; ~1 x 10⁸ γ/cm²-sec
$ D, T$ generator; ~1 x 10⁸ γ/cm²-sec
0 5-min irradiation, 1-min decay
* 10-min irradiation, 5-min decay
$ 30 $-min irradiation, 5 min decay
$ 20 $-min irradiation, 5 min decay
$ 3 $-min irradiation, 5 min decay

Titanium in Gun Powder Residues

The reduction of gun erosion by the use of additives to the gun powder has been studied at the US Naval Ordnance Station (NOS), Indian Head, Md. During the investigation of one of the additives, namely titanium dioxide (TiO₂) or Swedish additive, it was necessary to determine small amounts of Ti in gun powder residues taken from the gun after firing. As only very small amounts of Ti were expected in the samples, the very sensitive technique of NAA was used for the analysis (Ref 2)

Thermal neutron activation was selected for the radioassay via the ⁵²Ti(n,γ)⁵³Ti reaction. Since the half-life of ⁵³Ti was 5.8 min, non-destructive NAA by gamma-ray spectrometry was used in lieu of chem sepn of Ti

Gunpowder residues containing Ti were obtained after a gun firing by wiping the barrel with small pieces of wet cotton cloth. These pieces of cloth, containing the powder residue, were then irradiated together with clean pieces of the same size serving as blanks, and with a standard sample of TiO₂. Irradiations were performed in the Naval Research Laboratory reactor. The samples were packed in polyethylene bags, placed into polyethylene transfer "rabbits", and irradiated in the pneumatic transfer system of the reactor. In this way they could be transferred after irradiation to the counting location in about 1 to 2 min

⁵¹Ti was identified and counted by measuring the 0.32 MeV gamma-rays with a 4.45 x 5.08 cm Na iodide detector and a single-channel analyzer. Counting started usually 2 min after the end of an irradiation, and was carried out for about 60 min (about 10 half-lives), after which all the ⁵¹Ti activity had disappeared. The amount of Ti in the cloth samples was obtained by comparing the activities with that of the standard sample.

From the amount of TiO₂ added to the powder charge, from the length of the gun barrel, and from the weight of cotton cloth pieces, it was calculated that approx. 400 mg TiO₂ should be found on the cloth pieces after a gun firing, assuming even distribution of TiO₂ in the barrel. The sensitivity for TiO₂ detection by the NAA method was calculated as 0.3 mg. Within this limit, based on the NAA results obtained, no TiO₂ was detected in the gun barrel. The NOS workers concluded, therefore, that the material is "cleaned out" after each gun firing, i.e., there is no TiO₂ in the residue

2) Determination of Pellet Weight in Primers

Malfunctions of small arms ammo using the M34 primer have been related to inadequate control of pellet wt in the primer, with low pellet weight causing hangfires in the weapon. At the Army Mechanics and Materials Research Center (AMMRC), Watertown, Mass., NAA was investigated for 100% inspection of pellet wt in such primers (Refs 5 & 6)
Fig 4 is a sketch showing the components of typical primer caps for small arms cartridges. Wt specifications, in grains for the components of the M34 primer, with the various ranges and tolerances allowed in its manuf are as follows:

- Entire unit: 5.430–0.520
- Cup (Copper): 3.5 ± 0.15
- Anvil (Copper): 1.07 ± 0.07
- Disk (paper): Negligible
- Pellet Weight (individual): 0.600–0.120
- Pellet Weight (av of 5): 0.580–0.80

Fig 4  Components of Primer Cap for Small Arms Cartridges

Specifications for the primer pellet compn (FA-956) used in M34 primers are: Pb Stypnate 37 ± 5%, Tetracene 4 ± 1%, Ba nitrate 32 ± 5%, Sb sulfide 15 ± 2%, Al powder 7 ± 1%, PETN 5 ± 1%, and light gum soln as a binder (concn unspecified).

Two NAA methods were developed by AMMRC for non-destructive determination of pellet wt, both utilizing 14 MeV neutrons. In one method, total oxygen in pellet is determined via the 16O(n,p)16N reaction. Oxygen is present in the average pellet mix in a concn of 26.53% from the compds Ba nitrate, Pb Stypnate, Tetracene and PETN. Activation with fast neutrons yields 16N with a half-life of 7.2 sec and a 6.1 MeV gamma ray; 16N decomp to the original 16O. Total oxygen in a pellet was determined by irradiating a primer and a lucite standard under identical conditions (Ref 6), and counting both reference and sample simultaneously with two 12.7cm x 12.7cm NaI detectors. The gamma radiation from 16N was counted in an energy window from 4.85–8.0 MeV. From the measured oxygen content, pellet wt of a primer is calcd from the assumption that 0.159 grains of O are equivalent to 0.600 grains of primer pellet (based on the average oxygen concn of 26.53% in the pellet mix).

The other method for quality assurance inspection of pellet wt in the primer eliminates the need for a comparator oxygen-containing standard. Here, the Cu in the cup-anvil combination in the primer is used as an internal standard by comparing the 0.511 MeV positron annihilation radiation from 62Cu produced by the 63Cu(n,2n)62Cu reaction to the 6.1 MeV γ from 16N produced by oxygen activation. In this case the actual determination of pellet wt is not required; the ratio of Cu to O, which should be fixed for a pro-

To determine the Cu/O ratio, the outputs from the two linear amplifiers (one for each 12.7cm x 12.7cm NaI detector) were combined in a sum invert amplifier, the output of which was split and connected to two separate single-channel analyzers. The energy window of one analyzer was set from 0.45–0.60 MeV to count the 62Cu, and the other was set from 4.85–8.0 MeV to count the 16N. The primer was irradiated, transferred, and dropped in place between the two detectors for simultaneous counting of each energy band. The output of each single-channel analyzer was fed to an individual timer-scaler combination. The calcs for this method are somewhat more complex than for the case where a standard comparator of the same isotope is used. In the energy range set on the analyzer for Cu, there is a real contribution due to Compton (scattered) radiation from the oxygen. This is a function of the oxygen concn and must be determined by analyzing a sample containing oxygen as the only element activated by 14 MeV neutrons,
eg, a CHO compd, to obtain the ratio of the O count in the 4.85--8.0 MeV window to the Compton count due to O in the 0.45--0.6 MeV window. Also, since the $^{62}$Cu and $^{16}$N have markedly different half-lives, 9.8 min and 7.2 sec respectively, it is necessary to correct the counts in each window back to No, which can be the counts either at the time when irradiation stops or when counting starts.

Table 6 shows results obtained on some special primers prepared at Frankford Arsenal containing various pellet wts as specified in the last column. The Cu/O ratios with and without Compton corrections are shown:

Table 6

Determination of Pellet Weight and of the Copper/Oxygen Ratio for Special Primers* (from Ref 6)

<table>
<thead>
<tr>
<th>Primer Designation</th>
<th>Oxygen</th>
<th>Pellet Weight Based on Corr. O Weight* *</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu-Comp 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>B-1</td>
<td>0.084</td>
<td>0.260</td>
<td>5.9574</td>
</tr>
<tr>
<td>B-2</td>
<td>0.069</td>
<td>0.204</td>
<td>5.8339</td>
</tr>
<tr>
<td>B-4</td>
<td>0.085</td>
<td>0.264</td>
<td>4.7959</td>
</tr>
<tr>
<td>C-1</td>
<td>0.119</td>
<td>0.394</td>
<td>4.6093</td>
</tr>
<tr>
<td>C-2</td>
<td>0.115</td>
<td>0.378</td>
<td>4.8203</td>
</tr>
<tr>
<td>C-3</td>
<td>0.112</td>
<td>0.366</td>
<td>4.5599</td>
</tr>
<tr>
<td>D-1</td>
<td>0.170</td>
<td>0.585</td>
<td>2.5408</td>
</tr>
<tr>
<td>D-2</td>
<td>0.157</td>
<td>0.535</td>
<td>2.8207</td>
</tr>
<tr>
<td>D-3</td>
<td>0.159</td>
<td>0.545</td>
<td>2.9183</td>
</tr>
</tbody>
</table>

*Original Special Primers supplied by Frankford Arsenal
**Correction made for oxygen in primer cup, anvil, and paper

The pellet wt as determined by analysis for oxygen has been corrected for oxygen in the cup, anvil, and paper. Because the correction is indeterminable for individual primers, the oxygen correction of 0.015 grain is based on the mean wt values for cup, anvil, and paper, and is the same in all cases despite the fact that there may be a variation in individual cases. The expected trends are observed, namely, the lighter the pellet, the higher the Cu/O ratio. Doubling the pellet wt does not quite halve the Compton corrected ratio. The agreement between primers based on ratios is not as good as the agreement based on oxygen analysis as expected, because the ratio reflects the variation in cup and anvil wt as well as pellet wt. In the case of the lowest pellet wts, the ratios do not check as well as with primers having larger pellet wts, partly because of poorer statistics and partly because the effect of variations in cup and anvil wt will be a greater proportion of the total ratio.

In both the standard oxygen analytical procedure and the Cu/O ratio method, the primer was counted for 20 sec following a 25 sec irradiation and a 4.5 sec transfer from completion of irradiation to start of count.

Table 7 shows some typical results for production primers from East Acton, Illinois.

The pellets have been labeled WCC. The same information is reported as that in Table 6, with the addition of percentage deviations and the inclusion of primer unit wt. All the pellets fall within specification. The Cu/O ratios, both Compton corrected and uncorrected, essentially match the results of direct analysis, but there are discrepancies probably caused by the uncontrolled variances in other components of the primer such as the cup and anvil. In no case, however, is there a discrepancy in the ratios large enough to indicate pellet wt below specification, and so none of the primers tested in this group would be rejected on the basis of low pellet wt either by the Cu/O ratios.
or by direct O analysis. The primer unit wts (column 8) are quite uniform indicating relatively good overall quality control:

Table 7
Determination of Pellet Weight and Copper/Oxygen Ratios for Production Primers (from Ref 6)

<table>
<thead>
<tr>
<th>Primer Designation</th>
<th>Oxygen</th>
<th>Pellet Weight</th>
<th>% Dev. from Spec (0.600)**</th>
<th>% Dev. from Mean</th>
<th>Ratio</th>
<th>Primer Unit Weight</th>
<th>% Dev. from Spec (5.430)**</th>
<th>% Dev. from Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCC-1</td>
<td>0.168</td>
<td>0.576</td>
<td>-4.00</td>
<td>+1.59</td>
<td>3.178</td>
<td>4.699</td>
<td>5.171</td>
<td>4.76</td>
</tr>
<tr>
<td>2</td>
<td>0.169</td>
<td>0.581</td>
<td>-3.17</td>
<td>+2.47</td>
<td>3.161</td>
<td>4.653</td>
<td>5.126</td>
<td>5.60</td>
</tr>
<tr>
<td>3</td>
<td>0.172</td>
<td>0.594</td>
<td>-1.00</td>
<td>+4.76</td>
<td>2.812</td>
<td>4.304</td>
<td>5.107</td>
<td>5.89</td>
</tr>
<tr>
<td>4</td>
<td>0.173</td>
<td>0.596</td>
<td>-0.67</td>
<td>+5.11</td>
<td>2.642</td>
<td>4.133</td>
<td>5.163</td>
<td>4.92</td>
</tr>
<tr>
<td>5</td>
<td>0.155</td>
<td>0.530</td>
<td>-11.67</td>
<td>-6.53</td>
<td>2.920</td>
<td>4.411</td>
<td>5.209</td>
<td>4.07</td>
</tr>
<tr>
<td>6</td>
<td>0.160</td>
<td>0.547</td>
<td>-8.83</td>
<td>-3.53</td>
<td>2.818</td>
<td>4.310</td>
<td>5.212</td>
<td>4.01</td>
</tr>
<tr>
<td>8</td>
<td>0.170</td>
<td>0.584</td>
<td>-2.67</td>
<td>+3.00</td>
<td>2.599</td>
<td>4.091</td>
<td>5.136</td>
<td>5.41</td>
</tr>
<tr>
<td>9</td>
<td>0.165</td>
<td>0.565</td>
<td>-5.83</td>
<td>-0.35</td>
<td>2.679</td>
<td>4.171</td>
<td>5.226</td>
<td>3.76</td>
</tr>
<tr>
<td>10</td>
<td>0.171</td>
<td>0.588</td>
<td>-2.00</td>
<td>+3.70</td>
<td>2.545</td>
<td>4.037</td>
<td>5.118</td>
<td>5.75</td>
</tr>
<tr>
<td>11</td>
<td>0.151</td>
<td>0.513</td>
<td>-14.50</td>
<td>-9.52</td>
<td>2.954</td>
<td>4.446</td>
<td>5.167</td>
<td>4.84</td>
</tr>
<tr>
<td>12</td>
<td>0.164</td>
<td>0.563</td>
<td>-6.17</td>
<td>-0.71</td>
<td>2.727</td>
<td>4.219</td>
<td>5.185</td>
<td>4.51</td>
</tr>
<tr>
<td>13</td>
<td>0.165</td>
<td>0.567</td>
<td>-5.50</td>
<td>-0.00</td>
<td>2.669</td>
<td>4.161</td>
<td>5.204</td>
<td>4.16</td>
</tr>
</tbody>
</table>

*Correction made for oxygen in cup, anvil and paper
**M34 specifications

This feasibility study shows that determination of pellet wt by fast neutron oxygen activation analysis can be used for quality assurance inspection of M34 primers. Either direct oxygen analysis, where a comparison standard (such as lucite) is used, or a ratio method, utilizing the Cu in the cup-anvil combination as an internal standard, can be applied. In general, the uniformity of production primers is quite satisfactory; as is usually the case where production procedures are standardized. It seems likely that the light pellet is one which has been improperly manufd and will probably be well below specifications in pellet wt. Production experience with such primers indicates that only one in 3 x 10^8 primers is expected to show low pellet wt; therefore, one would not expect to find a reject in a small sampling. Nevertheless, detection and rejection of this one bad unit is critical for the prevention of weapon malfunctions and possible injuries to personnel.

As of this writing, 100% inspection by NAA of small arms primers in an actual production loading plant has not been implemented, nor is it contemplated in the near future. Technical problems exist related to coupling the present state-of-the-art nuclear components with the high production rates for the primers, namely, tens of units per sec per automatic loading line. The high intensity of the neutron source and the complexity of the detection system required detracts from the utility of the method in a plant environment where simplicity and safety of operation are of paramount importance. Nevertheless, the technical feasibility of the method has been demonstrated by the AMMRC study and future developments in nuclear activation hardware may ultimately make this non-destructive inspection for production primers more viable.
3) Determination of Gunpowder Residues in Forensic Investigations

In the field of forensic technology, there has long been a considerable need for detecting gunshot residues on the hands of an individual suspected of having fired a gun in a criminal act. The older technique for this purpose (Ref 8), variously referred to as the paraffin test, the paraffin-glove test, the dermal nitrate test, and the diphenylamine test, had been abundantly shown to be unreliable, was no longer accepted in most US courts, and was now seldom used by good crime investigation laboratories.

This older method involved: (a) coating most of the back of the hand of a suspect in a shooting case (or of the victim in a questionable gunshot-suicide case) with molten paraffin, (b) reinforcing the paraffin “cast” or “glove” with a few layers of gauze as the cast is made thicker, (c) peeling off the cast after it has solidified, (d) pouring some diphenylamine-sulfuric acid soln on the concave inside surface of the cast (that had been in contact with the skin), and (e) examining for blue specks imbedded in the paraffin. Thus, the dermal nitrate test is a color test for unburned or partially burned gunpowder, i.e., nitrocompds, which form a blue product with the acidic diphenylamine reagent.

In practice, it happens that the dermal nitrate test is not highly sensitive in that it does not develop a detectable blue color with very tiny particles of gunpowder. Also, it can apparently be interfered with in some cases by other material that may be present on a subject’s hand or in his perspiration, and the same color reaction can also be produced by various other nitrogen-containing compds, eg, fertilizers and urine.

In 1959, H.C. Harrison and R. Gilroy of the University of Rhode Island (Ref 1) reported on an improved gunshot residue detection method which also employed qualitative color reactions, but not with any gunpowder present on the back of the firing hand of a suspect. Instead, the method entailed detection of traces of particular elements that originated as constituents of the cartridge primer, viz, Ba, Sb, and Pb. Unfortunately, when various forensic laboratories attempted to use the Harrison and Gilroy method, they obtained very poor results. The chief problem appeared to be related to the fact that the method was being used at the limit of its sensitivity, i.e., the extremely small amounts of these elements deposited on the back of the gunhand in a typical firing was very close to the limit of the chemical detection method.

Early NAA Work at General Atomics Corp

In the early 1960’s, with the advent of high neutron flux NAA as an extremely sensitive method for the quantitative detection of many elements, the nuclear activation technique began to be investigated for determination of gunshot residues. The original preliminary experiments and much of the subsequent detailed investigations of this technique were performed at the General Atomics (GA) Corp, San Diego, Ca, by Vincent Guinn and his associates (Ref 8). The bulk of the material on determination of gunshot residues in this article is taken from the above.

The initial exploratory experiments at GA showed that the NAA approach worked quite well for the detection and measurement of Ba and Sb as primer residue elements. Since NAA sensitivity for Pb is rather poor, no effort was made to detect this third element. In these first experiments, the backs of both hands of a police officer were first rinsed with very dil nitric acid (after first washing his hands with ordinary soap and water), and the acid rinsings saved for analysis for background handblanks. The officer then fired a 0.38 cal revolver once, with his right hand, and the rinsing procedure was repeated. He then fired the same gun three times in rapid succession, again using his right hand, and subsequently both his hands were rinsed with dil nitric acid. The various nitric acid rinsings were then each placed in a small polyethylene vial, sealed, and irradiated for 30 min in a 250Kw TRIGA Mark I reactor, at a thermal neutron flux of 1.8 x 10^12 n/cm^2-sec. Because of the large amount of NaCl from perspiration present in the nitric acid rinses, it was observed that ^{24}Na and ^{38}Cl dominated the gamma-ray spectrum. As a result, activation products from other elements were masked out in using purely instrumental gamma-ray spectroscopy with an NaI scintillation detector. Radioactive Sb and Ba were therefore quantitatively separated chemically from the rinsings. In this manner, by counting the recovered Sb from each rinse, it was found that gross Sb on the gun-hand increased from 0.12 ug after one firing to 0.23 ug after three firings, with a background handblank...
before firing of 0.02ug and a reagent blank of 0.03ug. Similar results were obtained for Ba gunshot residues on the gun hand. Based on these encouraging results, more extensive investigations on use of NAA for this purpose were conducted by GA and other groups interested in forensic technology.

**Origin of Barium and Antimony in Primers**

The origin of Ba and Sb in commercial cartridge primers is typically from Ba(NO₃)₂ and Sb₂S₃ as constituents from the primer mix. Specific chem compn of a commercial brand is usually "proprietary" and not readily available. The GA investigators, upon analyzing residues from the firing of five different commercial brands of 0.38 cal ammo for total Ba and Sb, observed that anywhere from 49 to 334ug of Ba and from 16 to 168ug of Sb were collected. Quantities of Cu, presumably from the primer caps, in the range of 0.4 to 64ug were also observed.

The pertinent neutron activation data for the determination of Ba and Sb in gunshot residues by (n,γ) thermal neutron activation is given in Table 8

<table>
<thead>
<tr>
<th>Element</th>
<th>% Abundance</th>
<th>Thermal Neutron Cross Section, barns</th>
<th>Product Nuclide</th>
<th>Half-Life</th>
<th>Principal γ Photopeak, MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹³⁸Ba</td>
<td>71.66</td>
<td>0.35</td>
<td>¹³⁹Ba</td>
<td>82.9 min</td>
<td>0.166</td>
</tr>
<tr>
<td>¹²²Sb</td>
<td>55.25</td>
<td>6.5</td>
<td>¹²²Sb</td>
<td>2.80 days</td>
<td>0.564</td>
</tr>
</tbody>
</table>

At a thermal neutron flux of 1.8 × 10¹² n/cm²·sec and a 1-hr irradiation, experimentally-determined sensitivities for Ba and Sb are 0.0048ug and 0.0032ug, respectively. These sensitivities are reported to be adequate for the general gunshot-residue detection problem.

**Radiochemical Separation Procedure for Barium and Antimony**

As stated earlier, when gunshot residues are removed from the back of the hand of a person who has recently fired a gun, other material present on the skin, in particular considerable amts of Na chloride, are also removed, and that the activated Na and Cl products will dominate the pulse-height gamma-ray spectrum. The radiochemical separation procedure for Ba and Sb from the activated sample as developed by GA is as follows:

The activated sample is placed in a beaker, along with about 15ml of distilled water, 3.5ml of concd HCl, 1 ml of concd HNO₃, about 100mg of NaCl (as holdback carrier), and small amts (1 ml each) of carrier solns of Ba⁺², Sb⁺³, and Cu⁺² (20.0mg each), and the mixt boiled for 10 mins — to dissolve any particles present, and equilibrate any ¹³⁹Ba, ¹²²Sb, and ⁶⁴Cu present with their respective nonradioactive carriers.

After cooling, the soln is poured into a 50-ml centrifuge tube. One ml of concd sulfuric acid is added, and the soln is stirred to precipitate BaSO₄. The ppt is centrifuged, filtered on a preweighed filter paper, washed with water and then with ethanol, dried at 110°C for 15 mins, and weighed (thus determining the recovery of the Ba⁺² carrier). Cellophane tape is then placed over the ppt, and the filter paper is carefully folded and placed in a 2-dram polyethylene vial — the sample then being counted for its ¹³⁹Ba activity in a well-type NaI scintillation detector, coupled to a multichannel pulse-height analyzer. Copper is removed from the supernatant soln by adjusting the pH to 1.5–2.0 with NaOH soln, and extracting the Cu by shaking with 5ml of CHCl₃ soln of dithizone (400mg of dithizone in 100ml CHCl₃) in a 150ml separatory funnel. The lower (CHCl₃) phase is discarded. The Sb⁺³ in the supernatant soln left from the BaSO₄ pptn is pptd as Sb₂S₃, using about one gram of thioacetamide and heating. The ppt is centrifuged, dissolved in about 10ml of HCl soln, boiled for about 15 mins (to remove H₂S), cooled, and diluted to about 30ml. The free sulfur formed is centrifuged out. The supernate is transferred to a clean centrifuge tube, about 20ml of water and 2ml of chromous...
chloride soln (oxorbent) are added and stirred, and the tube is placed in a boiling water bath for 30 mins. The soln is allowed to stand overnight to complete the pptn and settling of elemental Sb, which is then transferred by means of a transfer pipette to a 2-dram polyethylene vial and counted for its $^{122}$Sb activity in a well-type NaI scintillation detector that is coupled to a multichannel pulse-height analyzer. The recovery of Sb carrier is determined by re-irradiation and comparing the resulting $^{122}$Sb activity with that of a similarly activated and counted comparator standard.

With the development of high resolution lithium-drifted germanium (Ge-Li) detectors in the late 60's and early 70's, for gamma-ray spectrometry, direct instrumental analysis for activated gunshot residues became more feasible. At a flux of $1 \times 10^{12}$ n/cm$^2$-sec for 3 hrs and counting directly with a 20 cm$^3$ Ge-Li detector connected to a 4096-channel analyzer, Borra et al (Ref 16) at the University of Pavia, Italy, report sensitivities for Ba and Sb as 0.05 ug and 0.01 ug, respectively. It should be noted, however, that these sensitivities are an order of magnitude lower, ie, poorer, than those obtained by GA's chem separation procedure.

Paraffin Coating Method for the Removal of Gunshot Residues from Hands
Various methods were investigated by the GA group for removing gunshot residues from the hands after firing a gun, including swabbing or scrubbing with different materials moistened with a variety of solns. Although these were convenient to use, unfortunately each showed very high levels of induced activities when activated in a reactor. The studies also showed that a swabbing or scrubbing technique, in general, did not remove as much gunshot residue-material from the skin as did a paraffin coating. A paraffin coating procedure was therefore adopted by the GA workers as the regular hand-sampling method to be used in all subsequent gunshot-residue work. Although not so convenient to apply, paraffin has the advantage of being readily available commercially in high purity, at a very low cost. Only the barest traces of Ba and Sb are found in most batches, thus resulting in an essentially negligible paraffin blank correction.

The application technique finally adopted by GA “consists of melting pure paraffin in a clean porcelain evaporating dish, holding the temperature at about 120°F, and then applying it to the desired region of the back of the hand, primarily the ‘thumb-web’ area, allowing the applied molten paraffin to cool and solidify, peeling it off, and placing all of the removed paraffin in a labelled polyethylene vial — ready for neutron activation. The person applying the paraffin is required to wash his hands carefully first, and then put on thin disposable plastic gloves, before proceeding. The molten paraffin is allowed to flow off of a small clean paintbrush onto the skin — rather than using a brushing or scrubbing motion — so that it is not transferred back to the dish of molten paraffin with repeated dippings of the brush into the dish. Naturally, a reasonably clean laboratory area must be used, and all materials employed must be free of barium or antimony. Measurements have shown that a second application of paraffin to a hand area, after the first lift has been peeled off, does not remove any significant additional amount of Ba or Sb.”

The “thumb-web” area, referred to in the above procedure is the V-shaped section formed by the surfaces on the back of thumb, the trigger finger and the area between the thumb and trigger finger. Controlled firing tests show that the bulk of the gunshot residues are deposited on this area of the back of the hand.

A distinctly negative factor on the utility of this method is the effect of washing the hands after firing a gun. It appears that normal washing of the hands destroys the evidence of a person having recently fired a gun. The length of time that has passed between the firing of the gun, the apprehension of the suspect and the performance of the residue test on the hands is therefore critical for the successful application of this technique.

Handblank Measurements
A highly important factor in the interpretation of gunshot residue analyses is the presence of either Ba, Sb or both on a person’s hands from sources other than the firing of a gun, eg, from materials encountered in their normal occupation. An extensive investigation of such handblank measurements was conducted by GA involving
Fig 5  192-Barium handblank values from 97 persons in 30 different occupations (from Ref 8)

Fig 6  188-Antimony handblank values from 97 persons in 30 different occupations (from Ref 8)
97 persons in thirty different occupations. Both the left and the right hand of each person was treated and assayed. In Fig 5, the measured handblank values for Ba for 97 people are presented in a logarithmic distribution form. The values do approximate a log-normal distribution. Fig 6 shows the corresponding data for the Sb handblanks. In this case, the possible log-normal shape of the distribution histogram is compressed at the lower-Sb end, because of the fairly numerous lesser values encountered, and many of these values were at or below the limits of detection. From all the values obtained, the median Ba was 0.20ug, and the median Sb value was about 0.010ug. No apparent correlation exists between the corresponding Sb and Ba values from the same person.

Table 9

<table>
<thead>
<tr>
<th>Weapon</th>
<th>No of Test Firings</th>
<th>Ba, ug</th>
<th>Low</th>
<th>Mean</th>
<th>Low</th>
<th>Sb, ug</th>
<th>High</th>
<th>Mean</th>
<th>Factor X Av Handblank Value</th>
<th>Ba</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 Cal Auto</td>
<td>32</td>
<td>0.216</td>
<td>15.4</td>
<td>3.60</td>
<td>0.068</td>
<td>3.12</td>
<td>0.598</td>
<td>6.9</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.44 Cal Rev</td>
<td>5</td>
<td>0.168</td>
<td>4.52</td>
<td>1.39</td>
<td>0.055</td>
<td>1.52</td>
<td>0.422</td>
<td>2.7</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.38 Cal Rev</td>
<td>79</td>
<td>0.168</td>
<td>12.7</td>
<td>1.31</td>
<td>0.045</td>
<td>4.17</td>
<td>0.421</td>
<td>2.5</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25 Cal Auto</td>
<td>4</td>
<td>0.96</td>
<td>8.46</td>
<td>4.72</td>
<td>0.208</td>
<td>1.26</td>
<td>0.632</td>
<td>9</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9mm Auto</td>
<td>5</td>
<td>1.37</td>
<td>15.4</td>
<td>7.47</td>
<td>0.056</td>
<td>2.05</td>
<td>0.732</td>
<td>14</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.22 Cal Auto</td>
<td>3</td>
<td>0.32</td>
<td>1.25</td>
<td>0.704</td>
<td>0.058</td>
<td>0.242</td>
<td>0.137</td>
<td>1.3</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.22 Cal Rev</td>
<td>16</td>
<td>0.21</td>
<td>0.82</td>
<td>0.391</td>
<td>0.05</td>
<td>0.24</td>
<td>0.082</td>
<td>0.75</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Handblanks</td>
<td>190^a</td>
<td>0.523</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0316</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a – Total No of individual measurements

Results of Test Firings

In Table 9, the results of Ba and Sb values from gunshot residue determinations by GA in 144 test firings are given. Seven different types of handguns were used including both automatic and revolver type weapons. One tentative conclusion that can be drawn from the relatively limited data is that larger-caliber guns generally seem to deposit more residue than do smaller-caliber guns.

It is also of interest to compare the mean Ba/Sb ratios from the test firings of the various guns with mean Ba/Sb handblank or background ratios. From the ~190 Ba and Sb handblank values, as shown in Figs 5 and 6, the mean Ba/Sb is 16.5. In all of the test-firing data, this ratio is much smaller, ranging from 3.12 for a 0.38 cal revolver to 10.2 for a 9-mm automatic. These ratios are not sharply defined — not only because of the numerous variables included even with a given caliber and type of gun (eg, make and condition of gun, chamber-fired in the case of revolvers, brand of ammo, wind direction and velocity, cartridge to cartridge variability within a single brand of ammo, reproducibility of the hand-area sampling technique, etc), but also because in many cases they include varying amounts of Ba and Sb already present on the hand before the test firing, ie, handblank material.

For the 0.45 cal automatics and 0.38 cal revolvers, sufficient test firings were performed to warrant some statistical analysis and interpreta...
Fig 7  Ba and Sb Values from 32 Firings of 0.45 Cal Automatics (from Ref 8)

Fig 8  Ba and Sb Values from 79 Firings of 0.38 Cal Revolvers (from Ref 8)
Table 10
Degree of Overlap of Firing Values with Handblank Values (from Ref 8)

<table>
<thead>
<tr>
<th>Type</th>
<th>No of Values</th>
<th>% of Ba Values &gt; 1.5ug</th>
<th>% of Sb Values &gt; 0.1ug</th>
</tr>
</thead>
<tbody>
<tr>
<td>Handblanks</td>
<td>97 persons</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>0.45 automatics</td>
<td>32 firings</td>
<td>66</td>
<td>94</td>
</tr>
<tr>
<td>0.38 revolvers</td>
<td>79 firings</td>
<td>27</td>
<td>90</td>
</tr>
<tr>
<td>0.44 revolvers</td>
<td>5 firings</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>0.25 automatics</td>
<td>4 firings</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>9 mm automatics</td>
<td>5 firings</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>0.22 revolvers</td>
<td>16 firings</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>0.22 automatics</td>
<td>3 firings</td>
<td>0</td>
<td>67</td>
</tr>
</tbody>
</table>

of the Ba values are > 1.5ug, but 90% of the Sb values are > 0.1ug. Thus, in this case, the degree of overlap with Ba handblank values is considerable, but the degree of overlap with Sb handblank measurements is fairly small.

The number of test firings with the other handgun types is too small to allow for much generalization. However, the degree of overlap of firing values with handblank values is summarized in Table 10 for all the weapon firings. It is evident from the table that, in almost every case, the Sb value provides a better distinction between a firing value and a handblank value than does the Ba value. It is also evident, at least from the above data, that it is very difficult to distinguish between a 0.22-cal firing (especially revolvers) and a handblank value.

Although the bulk of the work done on analysis of gunshot-residues was directed to the firing of handguns, at GA some measurements were also made on residues deposited from the firing of rifles and shotguns. Ba and Sb residues were analyzed for on the cheeks as well as on the hands of individuals. In general, little residues of these elements are found on the cheeks, but significant quantities above handblank values are observed on the firing hand.

Detection of Airborne Gunshot Residues

In addition to deducing whether or not an individual or suspect has fired a gun, in many criminological investigations the problem exists of determining where and when, or even if a weapon has been fired. Detection of gunshot residues on surfaces can pinpoint the location of the firing, but requires a systematic procedure covering many samples in suspect locations. These samples are inherently sensitive to contamination from accumulated dirt and dust lying on surfaces, and also can provide little or no time-of-firing information. At the Pennsylvania State University (Ref 17), a technique was developed to sample the gunshot residue left suspended in the air, followed by NAA to measure for traces of Ba and Sb. This method requires only one sample for suspected location, with external interference due mainly to the dust recently introduced into the air. Since the amount of residue remaining in the air is a function of time-after-firing, this technique also offers the potential of providing information as to the approx time the shot was fired.

A special test facility was constructed from polyethylene sheeting forming a 11½'x11½'x8' room suspended from an Al frame (Fig 9). A glove box is attached to one side to allow for revolver firing without disturbing the still-room environment. A carriage allows the revolver to be fired in the test room and then withdrawn into the glove box for loading and unloading. The target is a bullet catcher constructed from a 30-gal drum packed with cotton filler. An exhaust fan on one side allows for a complete change in room air between tests.
The results of test samples taken 4 hrs after firing, using the four major brands of 0.22 cal ammo available in the Eastern USA are shown in Table 11. These measurements demonstrate that

Table 11

<table>
<thead>
<tr>
<th>Ammunition</th>
<th>Sb\textsuperscript{b}</th>
<th>Ba\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western, .22 caliber</td>
<td>1.95 ± 0.75\textsuperscript{c}</td>
<td>5.12 ± 2.26\textsuperscript{c}</td>
</tr>
<tr>
<td>T-22 standard vel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remington Hi-Speed .22 caliber short</td>
<td>1.91</td>
<td>1.82</td>
</tr>
<tr>
<td>CCI .22 caliber</td>
<td>7.31</td>
<td>11.2</td>
</tr>
<tr>
<td>Imperial .22 caliber</td>
<td>17.6</td>
<td>21.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The region 1/2 to 4\textsuperscript{1} inches from the leading edge of the sample

\textsuperscript{b}Sampling time of 30 min, sampling started 4 hrs after firing

\textsuperscript{c}One standard deviation based on four test firings

Sb and Ba are present in the airborne gunshot residue expelled from all of the brands of 0.22 cal ammo. A chemical analysis of the primer of the Western brand gave a Ba to Sb ratio of 65, whereas the same ratio obtained from the data in Table 11 is 2.6. The authors conjecture that this additional Sb left in the air came from the vaporized bullet Pb which contains a large amount of Sb as a hardening agent.

Fig 10 shows the variation of airborne gunshot residue collected at various times after one firing. Following a general initial exponential fall-off, the rate of decrease slows at 48 hrs after firing. This is expected, since at these long times after firing, only the submicron gunshot residue particles remain suspended in the air. Under the "still" room conditions of these expts, these particles can remain suspended from weeks to months after firing.

The limiting sensitivity in this technique occurs in the analysis for Ba. Defining the limiting value as twice the standard deviation of the background In the 0.166MeV photopeak region, the least amount of Ba which can be detected is about 0.1 ug. Since the amount of Ba detected at 72 hrs is about 0.32 ug, and since Ba and Sb losses out of
Monitor was an approx one meter-wide area around
the hypothetical line parallel to the trajectory of
the bullet. Relatively large concns of residues were
found on the tract compared with other areas
farther from the trajectory.

Moistened filter paper (Whatman No 541) was
found to be optimum for collecting the residues
from floor surfaces. The filter paper squares con-
taining the powder residues were dried at 50°C
to remove moisture prior to reactor irradiation. Ba
and Sb standards were also prep'd to match the
geometry of the test samples, and were irradiated
under identical conditions.

The dry filter paper samples contained in poly-
ethylene vials were irradiated for 2 to 5 min at a
thermal neutron flux of $10^{13}$ n/cm$^2$·sec using the
pneumatic transfer system at the Penn State
TRIGA Reactor. Samples from 0.22 cal ammo
were usually irradiated for 5 min, while those
from higher cal ammo required only a 2 min ir-
radiation. The irradiated samples were transferred
to clean counting vials and counted with a 2 min
decay period. The short-lived isotopes of interest
were $^{139}$Ba (83.2 min), $^{122}$Sb (4.2 min) and
$^{60}$Cu (5.1 min). Instrumental radioassay was per-
formed with a similar nuclear counting system as
for the airborne gunshot residues (Ref 17) de-
scribed above with the addition of a programmable
computer coupled to the multichannel analyzer
for data processing. Using these procedures, it was
possible to detect Ba levels above $2 \times 10^{-9}$ g/cm$^2$
and Sb levels above $1.5 \times 10^{-9}$ g/cm$^2$ of floor surface.

Handguns tested ranged from a 0.22 cal to a
0.45 cal revolver. More specific details of the
firing expts and the range of results can be found
in the original ref. However, Figs 11 and 12 il-
lustrate some typical distribution patterns of Ba
and Sb produced on the floor of the 2.5 meter
long test facility from the firing of a 0.22 cal
revolver. These are smooth curves drawn thru the
analytical points to isolate areas of different
concn levels.

Firing tests with the other cal handguns indicated
distinguishable differences in the overall distribution
patterns of discharge residues from different
handguns. This unique distribution pattern of resi-
dues deposited immediately below the flight path
of the bullet results from the cloud of combustion
products emitted thru the barrel of the weapon.
The authors (Ref 20) propose the following
mechanism:

![Graph showing airborne Sb and Ba content in electrostatic precipitator samples as a function of time of firing](image-url)

**Fig 10** Airborne Sb and Ba Content in Electrostatic Precipitator Samples as a Function of Time of Firing (from Ref 17)

the air more than 48 hrs after firing are small
(Fig 10), it appears that under test conditions
the presence of gunshot residue could be detected
well beyond 72 hrs.

From the four hr test results, as given in Table
11, the variation of results with different 0.22 cal
ammo is indicated. Thus it would be difficult to
obtain precise time-of-firing information under
field conditions. However a gross estimate of this
time should be possible.

Firing tests conducted with larger than 0.22 cal
ammo showed that even greater sensitivity for de-
etection of Ba and Sb in airborne gunshot residues
can be obtained using these NAA techniques.

**Detection of Gunshot Residues on Floor Surfaces**

In another study at the Pennsylvania State
University (Ref 20), gunshot residues from firing
tests were assayed in order to establish distribution
patterns of Ba and Sb on surfaces below the flight
path of the bullet.

Test firings were conducted with handguns
using two different indoor ranges; one had a gun
to target distance of 2.5 meters while the second
had a 12 meter separation between gun and target.
The smaller facility maintained excellent control
over climatic conditions, whereas no control was
exercised with the large one. Both facilities
utilized soft penetrating materials as targets.
Thru the analysis (by NAA) of samples collected
from various points around the gun and target, it
was determined that the most desirable region to
When a projectile leaves the barrel of the gun at a high velocity, it sets up a wave front which extends out from the nose of the bullet. This condition creates an area of lower pressure immediately in its wake. In addition, due to the rifling action in the barrel of the gun, the projectile is discharged with a tangential velocity component. The combination of these two conditions creates a vortex in the wake of the bullet which carries with it some of the combustion products. Further, the continuous spinning of the bullet during its forward motion allows the spewing out of small amounts of combustion products within its wake. When the bullet hits the target, the wave front collapses, depositing all the remaining residues around the target. While this seems to be the mechanism by which the residues are carried farther from the gun, the major contributions to the residue patterns generated in the immediate vicinity of the firearm are the emissions from the barrel of the gun."

"On the basis of the above mentioned mechanism, a number of variables characteristic of a firearm (barrel length, location of the emission ports, and possibly by the twist of the rifling grooves) can influence the amount and nature of the distribution of combustion products. In addition, the size of the projectile, its shape and velocity can influence the amount of residue carried within the wake of the bullet and its distribution along the trajectory. The experimental observations made during this study generally substantiate the dependence of gunshot residue patterns upon the above mentioned characteristics of the weapon and the bullet."

Nondestructive NAA can thus be used for the detection and measurement of Ba, Sb (and also Cu) from residue samples collected from the floor surface after the single firing of a handgun. By constructing a unique distribution pattern of these residues, it is possible to establish the flight path of the bullet and the proximity of the gun with respect to the target. The development of this information, particularly in the absence of a firearm, a bullet or an eyewitness, can be of considerable value in criminal investigations.

*Experiments with Tagged Ammunition*

Because of the relatively high Ba and Sb hand-blank values found on persons in some occupations—which detracts from the reliability of the method for detecting gunshot residues on the hands of suspects—the idea was developed of deliberately tagging the gunpowder or primer material used in cartridges with low levels of very uncommon elements—using those that can be detected with extremely good sensitivity by NAA. As an aid to law enforcement, the approach here would have different US manufacturers of cartridges tag their gunpowder or primers with different combinations of these selected elements for each different type of cartridge. If technically and economically feasible, the use of tagged cartridges would offer several advantages: (a) the determination of whether or not a suspect had recently fired a gun...
would be more conclusive, (b) the analysis could also identify the brand and caliber of the cartridge fired, and (c) a completely instrumental radioassay procedure or a simpler radiochemical separation method would be more possible.

Rare earth elements, with relatively high thermal neutron activation cross-sections, have been tested or considered as tagging species for this purpose. At GA (Ref 8), preliminary expts were conducted with 0.38 cal ammo using dysprosium (Dy) and europium (Eu) deposited on the walls of the cartridge case and in the gunpowder, and Dy, holmium (Ho) and indium (In) in the primer. The amt of rare earth element used as a tag per round ranged from 1 to 100 µg. The results of expts were considered partially successful but inconclusive as to ultimate feasibility.

A more extensive investigation of rare earth tracers for this application is reported by Pillay et al (Ref 9) in which the high purity oxides of Dy and Eu were added to commercial "Bullseye" gunpowder at a level of 0.1 wt% and loaded into 0.45 cal cartridge cases. Test firings were carried out at an indoor pistol range and gunshot residues were analyzed from paraffin casts taken from the web, palm and back of both the firing and non-firing hands. Paraffin samples were irradiated in a reactor at a thermal neutron flux of 5 x 10^{12} n/cm^2-sec for 30 min and counted with a 3 x 3 in NaI scintillation detector both instrumentally, and also after radiochemical separation of the tracer elements.

Firing test results with Dy as a tracer were inconclusive in that there was an insufficient lack of discrimination between levels found on the firing and nonfiring hands. However, levels of Eu were significantly higher on the web of the firing hand; the percentage of Eu recovered in an individual firing averaged 0.02%.

The authors conclude that the use of Eu-labeled gunpowder can provide the basis for a rapid, simple instrumental gunshot residue test which can detect the firing of a weapon with a high degree of probability. The tagging of gunpowder with Eu can be developed into a method which is faster and less complicated than that based on the radiochemical separation of Ba and Sb with no reduction in sensitivity. An economic analysis based on a 0.1 wt% tagging level indicates the cost increase per box of cartridges at less than 2%.

4) Detection of Explosives in Buried Mines

The use of nuclear techniques for the detection of buried expts (in mines) has been investigated by the US Army over the past 25 years. The basic approach is the use of a direct beam of highly penetrating radiation to irradiate the soil and the measurement of a reflected, scattered, induced or secondary signal to indicate the presence of a buried mine. A complete historical review and analysis of this work has been prepared by Coleman et al (Ref 18). A brief summary of the highlights of the overall effort is provided here.

In the discussion that follows we refer to nuclear activation detection reactions in lieu of analysis reactions since the signals that are measured are not necessarily always from a radioactive product. Again, we will use standard nuclear physics notation in specifying nuclear reactions, namely:

\[
\text{target nucleus} \rightarrow \text{bombarding product} \rightarrow \text{product radiation(s)} \rightarrow \text{nucleus}
\]

Thru 1967, emphasis was given to the use of neutrons as the bombarding source of radiation. Almost all possible neutron reactions were considered including moderation of fast neutrons by hydrogen in the expl, thermal capture reactions, elastic and inelastic scattering of neutrons and neutron activation reactions. These neutron reactions are listed as follows:

- Fast neutron moderation: \( H(n,n')^1H \)
- Elastic scattering: \( ^{12}C(n,n')^{12}C, ^{14}N(n,n')^{14}N \)
- Inelastic scattering: \( ^{12}C(n,n'\gamma)^{12}C, ^{14}N(n,n'\gamma)^{14}N, ^{16}O(n,n'\gamma)^{16}O, ^{28}Si(n,n'\gamma)^{28}Si \)
- Thermal neutron capture: \( ^{14}N(n,\gamma)^{15}N \)
- Fast neutron activation: \( ^{14}N(n,2n)^{13}N, ^{28}Si(n,p)^{28}Al, ^{16}O(n,p)^{16}N \)

Of these neutron interactions, those that produce prompt-\( \gamma \) rays were evaluated as the most feasible for mine detection. As discussed in the Introduction, we define a prompt \( \gamma \)-ray as one which is produced as a direct result of the primary neutron interaction, usually within nanoseconds of that initial event. Such reactions are obviously attractive because they can best satisfy the desired rapid sweep rate over a minefield. The three specific neutron-prompt gamma reactions that were intensively investigated by the US Army are listed below:
<table>
<thead>
<tr>
<th>Nuclear Reaction</th>
<th>Eγ, MeV</th>
<th>Cross-Section, millibarns</th>
</tr>
</thead>
<tbody>
<tr>
<td>12C(n,γ)12C</td>
<td>4.43</td>
<td>160</td>
</tr>
<tr>
<td>28Si(n,γ)28Si</td>
<td>1.78</td>
<td>Large</td>
</tr>
<tr>
<td>14N(n,γ)14N</td>
<td>10.83</td>
<td>80</td>
</tr>
</tbody>
</table>

The first two reactions, which entail inelastic scattering of fast neutrons, in combination formed the basis of a thoroughly studied detection scheme. This method is based upon an increase in the 4.43 MeV γ-ray signal from carbon when over a mine and a corresponding decrease in the 1.78 MeV γ-ray signal from silicon in the soil. The laboratory research model developed for this scheme used the ratio of the two γ-ray signals to indicate the presence of a mine buried in the soil. The third reaction is based on the measurement of the 10.83 MeV γ-rays from thermal neutron capture by nitrogen in expls.

The chief obstacle to the neutron-prompt γ approach is that the specific γ-ray signal must be measured in the presence of a very high competing background signal. This background radiation is a combination of the signal emanating directly from the neutron source (either a neutron generator or an intense radiisotopic neutron emitter) to the detector and the host of prompt gammas produced from neutron interaction with all the other elements present in the soil, expl and detector components. The presence of this competing background places a stringent requirement on the resolution of the γ-ray detector, the complexity of the associated nuclear counting electronics and the amount of shielding required for the detector. When projected to an actual vehicle-mounted device, some of the laboratory model research mine detectors based on these schemes approximate fairly sophisticated nuclear physics laboratories on wheels. In addition, even with optimized laboratory research equipment, none of the prompt-γ schemes can detect mines efficiently beneath 2 or 3 inches of soil. The neutron-prompt γ approach is, therefore, considered not feasible for mine detection with present available nuclear technology.

Neutron activation reactions have also been considered for mine detection. Here a radioactive element is produced in the mine which in the process of decay, emits nuclear radiation, either alpha or beta particles or γ-rays or two of these or all three in combination. For buried mines the penetrating γ-rays are of most interest. In organic expls, the only elements capable of being so activated are nitrogen and oxygen. Using 14 MeV neutrons from a neutron generator, nitrogen via 14N(n,2n)13N produces 13N with a half-life of 10 minutes and a γ-ray energy of 0.51 MeV; oxygen via 16O(n,p)16N produces 16N with a half-life of 7.5 seconds and a 6.1 MeV γ-ray. Activation by fast neutrons of silicon in the soil, via 28Si(n,p)28Al to produce 2.3 minute 28Al (E 1.78 MeV) has also been considered for mine detection. This last approach will obviously not serve to give a direct signal for the presence of expls but can indicate the presence of a void or disturbance in the natural soil terrain by a reduction in the 1.78 MeV γ-ray signal. However, the nuclear parameters — cross-section, half-lives, interfering reactions, personnel shielding and neutron source requirements, etc. — are such that none of the above activation schemes are feasible for detecting mines with any degree of efficiency approaching military requirements.

In more recent years, γ-ray scattering techniques have been considered for buried mine detection. As an initial source of bombarding energy, γ-radiation is more attractive than neutrons because it is easily available in the form of relatively inexpensive long-lived radioisotopes. The more important ones (with their corresponding half-lives and principal γ-emissions are: americium-241 (438 yrs, 0.060 MeV), cesium-137 (30 yrs, 0.662 MeV), and cobalt-60 (5.2 yrs, 1.1, 1.3 MeV).

For γ-ray energies below 1 MeV (the range of interest) there are two principal modes of interaction with matter — Compton scattering and photoelectron absorption. Compton scattering is the elastic scattering of the γ photon by an orbital electron in which part of the incident γ energy is imparted to the recoiling electron. The number of Compton scatters occurring in a given volume depends on the number of electrons present and is relatively independent of incident γ-energy. For the lower atomic number elements (excluding hydrogen), the number of electrons present is directly proportional to atomic wt. Thus Compton scattering on a per unit volume basis is a function of density and is independent of chem compn. The density of soils is widely variable and the density of expls falls within the normal range of soil
density variation. Therefore Compton scattering alone does not provide a means of detecting mines, although it may provide a means of detecting expls in a more homogeneous matrix.

Photoelectron absorption is the total absorption of an incident photon by an orbital electron (predominantly the k electron), resulting in the freeing of that electron from its bound state. Photoelectric absorption is a strong function of gamma-ray energy (decreasing as roughly $E^3$) and of the atomic number (increasing roughly as $Z^4$ for the energy range of interest). Observing the number of photoabsorptions in a given volume therefore does provide a means of differentiating between soil, which has an average $Z$ of approx 11, and expls, which have an average $Z$ of approx 5. Unfortunately, photoelectric absorption cannot be detected directly as the photoelectrons produced are readily absorbed by the surrounding medium. However, while neither the Compton effect or the photoelectric effect by itself provides sufficient basis for the development of a viable expls detector, a combination of both effects will. While the fraction of total $\gamma$-rays Compton scattered in a volume of soil or expl is a constant, the total number of $\gamma$-rays available for Compton scattering is inversely proportional to the number of $\gamma$'s photo-absorbed. Consequently, proportionally more $\gamma$'s are scattered from a volume of expl than from a volume of soil. It is this increase in scattering that is detected, and this approach has been the basis for a number of devices designed to detect buried mines. However, soil penetration is relatively poor for the 60–100 keV $\gamma$-rays required in these devices, thus limiting their utility to shallow burial depths.

As of this writing, the overall assessment of the feasibility of nuclear techniques for detecting buried mines is poor, for the reasons discussed above.

5) Detection of Hidden Explosives in Baggage

The increasing use of expls for terrorist and political blackmail activities, in particular the international "skyjacking" incidents of the early and middle 1970's, has resulted in a great interest in the development of efficient technological methods for detecting hidden expls, eg, in airline luggage. A technique that has received considerable attention for this purpose is the irradiation of luggage or suspect packages with fast neutrons followed by measurement of the $\gamma$-radiation from activated expl if present in the item. The approach is based on the same nuclear activation reaction discussed above under Elemental Analysis for total nitrogen content determination by FNAA, namely, the $^{14}$N(n,2n)$^{13}$N reaction with 14 MeV neutrons, and counting of 0.511 MeV annihilation $\gamma$-rays emitted from the decay of $^{13}$N. The potential success of the method is dependent on the premise that most expls contain nitrogen in varying amounts — in quantities greater than in the usual items found in passenger baggage. Mercury Fulminate has as little as 9.8 wt% of nitrogen and PETN as much as 56 wt%. A stick of straight Dynamite contains 15 wt% of nitrogen.

As discussed previously, when an expl is irradiated with fast neutrons a $^{14}$N nucleus captures the incident fast neutron and emits two slow neutrons. The resulting nucleus, $^{15}$N, is excited (radioactive) and decays with a 10 min half-life to stable $^{13}$C. In this last transition, a positron, $\beta^+$, is emitted. Because of its opposite charge, the $\beta^+$ is strongly attracted by a nearby electron; in the resulting collision, both the positron and electron are annihilated and in the process of annihilation, the masses of the colliding particles are converted into two 0.511 MeV quanta of electromagnetic radiation. These $\gamma$-rays are what are detected to indicate the possible presence of an expl.

Using the above neutron activation scheme, the North American Rockwell Corp (Los Angeles), under contract to the US Federal Aviation Administration (FAA), developed a full-scale operational system to test its feasibility for automatic inspection of airline luggage for the presence of expls (Ref 10). A block diagram of the activation concept employed in a baggage handling environment is illustrated in Fig 13. A conveyor belt transports luggagefirst past a neutron generator and then past a detector. The radiations detected are amplified, analyzed, and compared with a preset threshold. If the detected radiations surpass the threshold, a visual alarm is activated.

A sealed-tube neutron generator, utilizing the deuterium-tritium reaction is the source of fast (14 MeV) neutrons, and a 8" x 3" NaI scintillation detector, with three optically coupled photomultipliers, is used to measure the $\gamma$-ray signal.
For the presence of hidden explosives (from Key 10)

Figure 13: Fast Neutron Activation System for Inspection of Airline Baggage

Diagram showing components such as supply, power system, control system, detector, and irradiation.
from each item of irradiated luggage. Both generator and detector stations have to be heavily shielded by a combination of concrete and lead. Shielding of the generator is necessary to protect the outside environment from harmful levels of radiation, and the detector must be shielded to maintain background levels as low as possible to maximize signal to noise ratio. The pulse height analyzer counting system isolates the desired 0.511 MeV γ-ray signal from other radiations.

Typical demonstration expts with this system consist of filling handbags or suitcases with items customarily carried by passengers and placing these bags on the conveyor belt. Each bag is passed over the neutron generator and subjected to a total fast neutron fluence (integrated dose) of $10^8$ neutrons/cm$^2$. After approx 25-sec delay, the bag passes under the scintillation detector, and the time-history of the radiation levels from the bag are recorded by the nuclear counting system. Integrated count times for a single bag are in the order of 2 sec.

Next, the bags are opened and up to six sticks of straight Dynamite (or other type of expl, eg, Ammonium Nitrate) are placed inside, and the irradiation-count procedure is repeated. Typical results with sticks of 45% Gelex straight Dynamite, $1\frac{1}{4}$" x 8" cylindrical, approx 200g per stick, are shown in Table 12. (The designation "45% straight" refers to the expl strength of the Dynamite relative to blasting gelatine, rather than to its chem compn). Background counts are subtracted for the peak count rates given.

**Table 12**

<table>
<thead>
<tr>
<th>No of Sticks</th>
<th>Peak Counts/Sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>130</td>
</tr>
<tr>
<td>5</td>
<td>160</td>
</tr>
<tr>
<td>6</td>
<td>190</td>
</tr>
</tbody>
</table>

The results in Table 12 are considered very conservative by the North American Rockwell authors, since they were not obtained under optimum conditions. Such conditions must take into account the type of luggage, conveyor belt speed, detector size, type of signal processing and activation geometry. None of these factors was optimized in the demonstration system. The authors project that the system as assembled could reliably detect a min of two sticks of straight Dynamite or one stick of Ammonium Nitrate.

Another way of demonstrating currently achievable performance with the above system is shown in Table 13. Here, the peak counts/sec from a typical empty suitcase, leather attach case, and the leather attach case containing six sticks of Dynamite are compared to the background level. The attach case, in both cases, was also filled with common nitrogen-rich materials such as wool, vitamins B$_1$ and B$_2$, pills, rayon, saccharin, silk and other materials such as paper, cotton and brass.

**Table 13**

<table>
<thead>
<tr>
<th>Count Rate of an Attache Case Filled with Dynamite vs Background Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Room Background</td>
</tr>
<tr>
<td>Typical Empty Suitcase</td>
</tr>
<tr>
<td>Leather Attache Case (Filled)</td>
</tr>
<tr>
<td>Leather Attache Case (Filled) + 6 Sticks of Dynamite</td>
</tr>
</tbody>
</table>

From the data in Table 13 it is apparent that the signal from an item of luggage containing as many as six sticks of Dynamite is not sufficiently above the range of background levels to make the detection of smaller quantities of expl highly reliable. Materials, other than expls, which also contain nitrogen, will of course reduce detection reliability by increasing the false alarm rate.

Any element which emits radiations similar to that of nitrogen, when activated with fast neutrons also represents a potential source of false alarms. Even elements which emit radiations with higher energy γ-rays than that of nitrogen represent a source of false alarms, since these higher energy γ-rays degrade to the 0.511 MeV level thru inelastic collisions (Compton scatter). The element most commonly found in baggage which is a likely source of false alarms is Cu — as present in articles containing brass. The interfering reaction here is $^{63}$Cu(n,2n)$^{62}$Cu; the activated Cu product also decays by positron emission resulting in 0.511 MeV γ-rays, and its half-life is 9.7 min — almost identical to the 10 min half-life of $^{15}$N.
Although the North American Rockwell system was never optimized for max performance, the authors claim that sufficient demonstrations were run to verify feasibility. Four sticks of Dynamite were repeatedly detected in luggage with a probability of detection greater than 90%. Approx one false alarm per 1000 detections was noted which corresponds to better than $3\sigma$ false alarm rate. This false alarm rate, however, becomes much greater as one attempts to detect a smaller quantity of expl, ie, less than 4 sticks of Dynamite.

Consideration has also been given to the possible harmful effects of the irradiation treatment on consumable materials present in luggage — either from induced radioactivity or radiation damage. For an integrated 14 MeV neutron dose of $10^8 n/cm^2$ on a suitcase, radiation induced by activating products such as foodstuffs, cosmetics, contraceptive devices, clothing and other personal items are assessed as being insignificant (Ref 12). Ordinary photographic film is also apparently visually undamaged when exposed to the neutron dose (Ref 10).

In 1972, the Lawrence Livermore Laboratory (LLL), also under Contract to the FAA, published a report (Ref 15) describing a more detailed statistical and experiassessment of this same fast neutron activation method for inspecting baggage for the presence of expls. The LLL approach was directed towards a more quantitative evaluation of the nitrogen content background likely to be encountered in ordinary passenger luggage.

Table 14

Comparison of % N by Weight in Some Materials Found in Typical Luggage and in Explosives (from Ref 15)

<table>
<thead>
<tr>
<th>Material</th>
<th>wt % N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>0.0</td>
</tr>
<tr>
<td>Wool</td>
<td>16.0</td>
</tr>
<tr>
<td>Leather</td>
<td>18.0</td>
</tr>
<tr>
<td>Fur</td>
<td>16.0</td>
</tr>
<tr>
<td>Silk</td>
<td>18.4</td>
</tr>
<tr>
<td>Nylon</td>
<td>10.0</td>
</tr>
<tr>
<td>Rayon</td>
<td>0.0</td>
</tr>
<tr>
<td>Orlon, Acrylic</td>
<td>26.4</td>
</tr>
<tr>
<td>Dacron &amp; similar polyesters</td>
<td>0.0</td>
</tr>
<tr>
<td>Dynamite</td>
<td>15-30</td>
</tr>
<tr>
<td>TNT</td>
<td>18.4</td>
</tr>
<tr>
<td>RDX</td>
<td>37.7</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>35.0</td>
</tr>
</tbody>
</table>

Items and its influence on the false alarm rate for a particular threshold setting. The compn of items most commonly contained in luggage was considered, the most important being clothing, typically made from natural and synthetic fibers in various combinations. The nitrogen content of common synthetic and organic fibers are compared to some standard commercial and military expls in Table 14 and it is seen that the N contents of some of these are in the same range as those of expls.

In Table 15, the compn and N contents of specific items of clothing are given, and the LLL workers have also estimated the N content equivalency in terms of sticks of Dynamite (where one stick of Dynamite is taken to contain 20g of N).

From the data in Table 15, the LLL authors estimate that over half the suitcase population being processed at an airline terminal will contain the same amt of nitrogen, plus or minus a pair of shoes or a sweater. Then, a conservative estimate of the standard deviation of the nitrogen distribution may be put at 100g of N. This means that in order to have a false alarm rate of no more than 0.13%, or $3\sigma$ above the mean, the N threshold must be set at more than 300g above the average. With this threshold, an extra 300g of N is detected 50% of the time, and the additional N content due to expls must go to 500g in order to be detected with 98% probability. This would represent as much N as in 25 sticks of Dynamite (at 20g per stick).

Experl irrations were performed at LLL to study and demonstrate the response of the fast neutron activation system to background nitrogen, and elemental interferences as applied to measuring gross nitrogen in a suitcase for the detection of hidden expls. The suitcases contained various clothing articles and nylon rods were used as mock Dynamite. A Kaman Nuclear A711 sealed tube generator with a total output of $4.5 \times 10^{10} n/sec$ was the source of 14 MeV neutrons. Suitcases were introduced by hanging them on a trolley which ran near the generator target. During irradiations the suitcase was stationary at a distance of 40cm from the neutron source. Irradiations were performed at full power for 60 sec, and the integrated neutron flux seen by the sample was $5.4 \times 10^8 n/cm^2$. The activated suitcase was then passed over two 2x8" NaI scintillation detectors, positioned side by
Table 15
Nitrogen Content and Dynamite Equivalency of Selected Items of Clothing
(from Ref 15)

<table>
<thead>
<tr>
<th>Item</th>
<th>Composition</th>
<th>N Content</th>
<th>N Content Equivalency as Sticks of Dynamite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Socks</td>
<td>% Orlon, % Nylon</td>
<td>12.5</td>
<td>5/8</td>
</tr>
<tr>
<td>Sweater</td>
<td>Acrilan</td>
<td>105</td>
<td>5 1/4</td>
</tr>
<tr>
<td>Sweater</td>
<td>Orlon</td>
<td>104</td>
<td>5 1/4</td>
</tr>
<tr>
<td>Shirt</td>
<td>Orlon</td>
<td>75</td>
<td>3 3/4</td>
</tr>
<tr>
<td>Blazer</td>
<td>Wool</td>
<td>190</td>
<td>9 1/2</td>
</tr>
<tr>
<td>Jacket</td>
<td>Nylon</td>
<td>25</td>
<td>1 1/4</td>
</tr>
<tr>
<td>Shoes</td>
<td>Leather</td>
<td>164</td>
<td>8 1/5</td>
</tr>
<tr>
<td>Bodyshirt</td>
<td>Nylon</td>
<td>14.2</td>
<td>7/10</td>
</tr>
<tr>
<td>Pantyhose</td>
<td>Nylon</td>
<td>5</td>
<td>1/4</td>
</tr>
<tr>
<td>Nightwear</td>
<td>Nylon</td>
<td>31.2</td>
<td>1 1/2</td>
</tr>
<tr>
<td>Panties</td>
<td>Nylon</td>
<td>8.5</td>
<td>2/5</td>
</tr>
<tr>
<td>Slips</td>
<td>Nylon</td>
<td>14.1</td>
<td>7/10</td>
</tr>
<tr>
<td>Dresses</td>
<td>Nylon</td>
<td>25.5</td>
<td>1 1/4</td>
</tr>
<tr>
<td>Shorts</td>
<td>Nylon</td>
<td>22.7</td>
<td>1 1/8</td>
</tr>
<tr>
<td>Overcoat</td>
<td>Wool</td>
<td>218</td>
<td>10 4/5</td>
</tr>
</tbody>
</table>

side, and the outputs summed to produce a single pulse height spectrum in a multichannel analyzer counting system. Counts were taken for 200 sec after a delay of 120 sec from the end of the irradiation period.

A typical γ-ray spectrum from an Al (the most popular fabrication material) suitcase is shown in Fig 14. The neutron-activated Al decay peaks are indicated in addition to the 511 keV peak from 12N. Although not an interference in detecting the nitrogen γ-rays, the Al γ-rays mask higher energy γ's from Cu and other interfering elements which can also contribute to the nitrogen signal.

Based on the initial statistical analysis and subsequent exptl verification, the following summary and conclusions are made in the LLL report:

"The feasibility of the fast neutron bulk activation detection system and of other bulk nitrogen measurement systems is in serious question. The nitrogen present in innocent, common, and completely legitimate materials to be found in suitcases varies sufficiently that the estimated minimum detectable amount of explosive in this system is around 25 to 50 sticks of '40% straight dynamite' (containing 20 grams of nitrogen per stick, although some types of '40% straight dynamite' contain as much as 50 grams of nitrogen per stick). This is a much greater amount than the desired minimum of 3 to 4 sticks. These limits are determined by the estimated variation in nitrogen content of the suitcase population and are independent of the nitrogen measurement technique itself."

"There are several activation techniques for measuring nitrogen in an unknown sample. One of them is to activate the sample with fast neutrons. The nitrogen is then activated in an n,2n reaction and subsequently decays with a 10 minute half-life. The annihilation gamma radiation of the positron decay product is detected. There are a great many elemental interferences to this technique. One elemental interference which is strong and seemingly indistinguishable from nitrogen in the presence of aluminum is copper. Copper is commonly found in a variety of items such as electric shavers, brass snaps, and zippers. To remove this interference, an associated technique such as x-ray radiography could be used to look for copper articles. Also high-maintenance, high-resolution germanium detectors might allow the weak higher energy copper gamma rays to be distinguished from the ever-present aluminum gamma rays."
Fig 14  NaI Scintillation Detector Pulse Height Spectrum of an Aluminum Suitcase Filled with Clothing (from Ref 15)
"The system studied which uses sodium iodide scintillation gamma ray detectors is not feasible for detecting four sticks of dynamite in a typical piece of passenger luggage. It is not feasible to measure the luggage’s nitrogen content, free from elemental interferences with the fast neutron technique. A threshold on the nitrogen level measured by any technique may not be set which allows both low false alarm rates and high detection probability for so small an amount of nitrogen.”

At PicArsn (Ref 19), the fast neutron activation approach for detection of expls in suitcases was extended to the activation of both nitrogen and oxygen using two γ-ray detector stations in sequence. After 14 MeV neutron irradiation, the baggage is first monitored for 6.1 MeV γ-rays from the $^{16}\text{O}(n,p)^{15}\text{N}$ reaction (7.5 sec half-life), followed by measurement of the 10 min $^{13}\text{N}$. Because expls are also rich in oxygen and have characteristic ratios of N/O, it was felt that this approach would increase the probability of detection with a corresponding decrease in the false alarm rate.

From exploratory expls with suitcases containing 800g of RDX and a variety of common materials such as cotton, nylon, brass, Na bicarbonate, etc, a greater reliability for expls detection was observed using the dual N and O signals. For example, where the nitrogen signal is masked by the presence of Cu in brass, the oxygen signal can indicate the presence of an expl. Likewise, where the presence of Na bicarbonate masks the oxygen signal, the nitrogen activity can signal a suspect bomb. However, the PicArsn workers conclude that the additional reliability introduced by the dual-signal approach is insufficient to alter the overall pessimistic assessment, drawn by LLL, as to the feasibility of the fast neutron activation technique.

The introduction of tight personal security procedures and visual or X-ray inspection of carry-on luggage at all domestic and international airports in 1972, resulted in almost complete elimination of “skyjacking” incidents in the USA. This situation has most likely interrupted or delayed the further development of automatic non-destructive inspection methods for expls in baggage at airline terminals.

6) Explosives Safety in Neutron Activation Analysis

This section will deal briefly with some aspects of expls safety peculiar to neutron activation analysis expls. We are concerned here with a) the possible effect of the ionizing radiation dose on the energetic material which will cause it to be more sensitive or hazardous to normal handling as an expl, and b) the potential direct expl hazards involved in the physical and mechanical transportation of samples to and from the irradiation source and in a nuclear counting system.

The effects of ionizing radiation on expls and related energetic materials have been well investigated over the years (see Radiation Effects on Explosives in Vol 9) and are quite predictable. The properties of such materials are not measurably altered until subjected to doses in excess of a million rads. At these higher doses, the principal changes are due to chem decompn which, with very few exceptions, result in a decrease in sensitivity to mechanical stimulus and also in a diminution of expl output. The radiation doses normally encountered in neutron activation procedures range from a few rads for 14 MeV fast neutron activation to several thousand rads for thermal neutron activations in a nuclear reactor. Thus, such doses are well under the limit at which measurable changes can occur.

With regard to the hazard concern from physical and mechanical handling, the expl nature of the materials can pose a special problem. For example, during pneumatic transfer of samples in fast neutron activation, the polyethylene vials containing the expl approach speeds of 15m/sec and come to rest against a metal stop at both irradiation and count stations. However at PicArsn (Ref 13), in over 1000 irradiations and pneumatic transfers with up to 2.3g of shock-resistant secondary expls such as TNT, HMX, RDX and Nitrocellulose, no detonation occurred. Similar experience has been reported at the US Naval Ordnance Station, Indian Head, Md (Ref 3) in over 100 irradiations with 40mg samples of RDX, HMX, anhydrous hydrazine and composite proplns.

On the other hand, for low shock-resistant expls such as Pb Azide, Mercury Fulminate or
Fig 15  Special Self-shielded Irradiation Cells for Fast Neutron Activation of Initiating Explosives

initiating agents, pneumatic transfer of samples is not recommended. Here, only manual transfer of samples to the target and back to the count station should be performed under the most careful handling conditions. At PicArsn (Ref 22) special irradiation cells have been designed to contain initiating expls for fast neutron activation. Each cell is a hollow aluminum cylinder, 5cm in height by 4.2cm in diam with 7mm thick walls, and contains a threaded Al cap. The unit is vented in the cap and also on the bottom wall, and is designed to hold a small polyethylene vial cushioned by two polyurethane discs. These cells can withstand the detonation of up to 200mg of Pb Azide without causing fragmentation, but in practice are only used for amts of initiating expl up to 100mg. For activation exps, 4 cells are mounted on a Delrin thermoplastic wheel, 10cm in diam by 5.7cm thick, contg 4 sample wells. Fig 15 shows a photograph of the entire assembly, with the wheel containing the 4 cells mounted on a motor for single-axis rotation in front of the target of a 14 MeV Kaman nuclear sealed-tube neutron generator. Since this system is designed for manual transfer of samples only, it is limited to the analysis of elements that yield activated products with half-lives longer than about 60 sec

Written by S. HELF

Nuclear Ammunition and Weapons. See Vol 1, A499-L to A500-L, A504-L to A505-R, and the following addnl refs

NUCLEAR COUNTING OF TAGGED EXPLOSIVES BY LIQUID SCINTILLATION

Because of their expl nature, the counting or radioassay of tagged expls can pose special problems with regard to safe manipulation. In particular, we are concerned here with expls such as TNT, RDX, HMX, NG, PETN, etc, tagged with low energy beta emitters such as carbon-14 and hydrogen-3 (tritium). Liquid scintillation (LS) counting has been developed over the past 20 years primarily for the radioassay of labeled biological samples in nuclear medical applications. At PicArsn this technique has also been applied successfully to the counting of radioactive expls (Refs 1, 2 & 4)

In the LS counting process, the radioactive sample is either dissolved or suspended in a special soln or gel system capable of producing visible light pulses upon interaction with the beta particles from the tracer atoms. These light pulses are then counted by conventional photomultiplier tube techniques. A LS system that has proven to be very popular for organic-soluble samples consists of the following: 4g of 2,5-diphenyloxazole (commonly called PPO) and 100mg of 1,4-di(2-(5-phenyloxazolyl))-benzene (commonly called POPPOP) in a liter of toluene. The scintillation-detection mechanism of this system is explained by Gardner and Ely (Ref 5) as follows: "

1) Solvent (toluene) molecules are excited by incident radiation;
2) Solvent-molecule excitation energy is transferred to the PPO molecules, often called the primary fluor or solute;
3) The PPO molecules go to the ground state via the emission of photons with average wavelength of 3700Å;
4) The 3700Å wavelength photons interact and excite the POPPOP molecules. The POPPOP in this case is called the secondary fluor or the wavelength shifter; and
5) The excited POPPOP molecules go to the ground state via the emission of photons with average wavelengths of 4200Å. These photons can be efficiently used to eject photoelectrons at the photocathode of the photomultiplier tube"

Expls tagged with $^{14}$C or $^3$H can be counted either in homogeneous soln with the scintillator system, or as a suspension of finely divided particles in a gel scintillator. These two methods are discussed separately below:

Homogeneous Solution Counting. This method is used for expls soluble in the toluene solvent. In practice, approx 50–200mg of sample, eg, TNT—$^{14}$C, is dissolved in 20ml of the toluene—PPO—POPPOP soln in an optically clear glass vial of 22ml capacity. In the early stages of this development (Ref 2), problems arose in attempting to radioassay tagged nitrocompds dissolved in the scintillator system not containing the secondary solute or wavelength shifter POPPOP. It was observed that nitrocompds served to markedly quench the scintillation process by restricting the light output and thus reduce counting efficiency. This is illustrated in Fig 1 in which eight different nitrocompds are compared with respect to relative counting efficiency as a function of concn in the toluene—PPO scintillator. In this exp, varying concns of each nitrocompd was added to the scintillator soln in which the toluene solvent was tagged with a fixed quantity of carbon-14. Counting efficiency is given as I/Io, on a semi-log scale, where I is the count rate for a particular concn of nitrocompd, and Io is the count rate of the pure scintillator (toluene—$^{14}$C—PPO). Each nitrocompd exhibits a characteristic attenuation of the counting rate of the pure scintillator soln. Moreover, the linearity of the data indicates a strong adherence to a Beer-Lambert exponential relationship.

Helf & White (Ref 2) interpret the above behavior of the nitrocompds in inhibiting the scintillation process as one of simple light absorption rather than as a true chemical quenching (de-excitation process). To substantiate this, the UV and near-visible spectrum of each of the light compds in toluene—PPO soln was measured using the 50% extinction concn for each nitrocompd (as determined from Fig 1). All of the compds exhibit a definite absorption peak in the UV region. These spectroscopic data are listed in Table 1. To fully correlate these light absorption data with the curves in Fig 1, consideration must be given to the emission characteristics of the pure scintillator. PPO in toluene (4g/l) has an emission range of 3400 to
Fig 1  Quenching of the Scintillation Process by Organic Nitrocompounds in Toluene—\(^{14}\)C—PPO

Fig 2  Quenching of Scintillation by p-Nitrotoluene in Toluene—\(^{14}\)C—PPO with and without POPOP

### Table 1. Absorption Data for Nitro Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc., Mmole per Ml(^a)</th>
<th>Absorption Peak, Å</th>
<th>Absorption Range, Å</th>
<th>% Transmission at Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trinitrotoluene</td>
<td>0.0040</td>
<td>3500</td>
<td>3380—4250</td>
<td>53</td>
</tr>
<tr>
<td>2,6-Dinitrotoluene</td>
<td>0.0052</td>
<td>3470</td>
<td>3380—4250</td>
<td>54</td>
</tr>
<tr>
<td>2,4-Dinitrotoluene</td>
<td>0.0060</td>
<td>3475</td>
<td>3380—4250</td>
<td>53</td>
</tr>
<tr>
<td>o-Nitrotoluene</td>
<td>0.0072</td>
<td>3510</td>
<td>3400—4250</td>
<td>60</td>
</tr>
<tr>
<td>p-Nitrotoluene</td>
<td>0.0078</td>
<td>3510</td>
<td>3390—4250</td>
<td>66</td>
</tr>
<tr>
<td>m-Nitrotoluene</td>
<td>0.0096</td>
<td>3500</td>
<td>3400—4200</td>
<td>68</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.0120</td>
<td>3480</td>
<td>3420—4250</td>
<td>66</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>0.0485</td>
<td>3150</td>
<td>2900—3850</td>
<td>98</td>
</tr>
<tr>
<td>1,1,1-Trinitroethane</td>
<td>0.0115</td>
<td>3625</td>
<td>3550—4100</td>
<td>97</td>
</tr>
</tbody>
</table>

\(^a\)Solutions contained in silica cells, 1 mm thick
4300 Å with a max at 3800 Å. The absorption overlap of the nitrocompds is plainly evident. The position and slope of each curve in Fig 1 can be qualitatively correlated with the absorption range and % transmittance at the peak for each compd. Nitromethane, which absorbs more at shorter wave lengths and exhibits the least overlap of the toluene—PPO emission spectrum, accordingly has the least effect on the count rate of the pure scintillator.

The addition of a secondary solute or wavelength shifter can serve to offset much if not all of the action of tagged nitrocompds in reducing counting efficiency. For expl nitrocompds, a shift of the emission spectrum considerably into the visible region where absorption effects are not so pronounced is clearly indicated. The secondary solute POPOP has been found to be most efficient for this purpose (Ref 2). This enhanced effect on the scintillation process is illustrated in Fig 2 for p-Nitrotoluene.

Expl compds tagged with 14C or 3H can be counted by homogeneous soln liquid scintillation with efficiencies approaching 90% and 50%, respectively, for unquenched systems (100% efficiency denotes that all beta particles emitted from a sample are counted). For organic nitrocompds, counting efficiency will be somewhat reduced due to partial absorption of light pulses as discussed above, but much higher than the 1–10% obtainable with end-window Geiger detectors.

Suspension Counting in Gel Scintillators. For tagged compds that are not soluble in toluene, one can resort to a technique whereby the solid sample, in finely divided form, is suspended in the liquid scintillator. By increasing the viscosity of the soln, the problem of particle settling can be eliminated. Al stearate was originally used to thicken toluene solns, and later Thixcin-R, a castor oil derivative, was introduced for the same purpose (Ref 1). The thickened, semi-transparent solns were referred to as gel scintillators. The two former thickening agents have since been supplanted by Cab-O-Sil (Ref 3), an aerated silica gel with a very high surface area of 200m^2/g. Cab-O-Sil gels, fluid enough to pour yet viscous enough to maintain stable suspensions, are prepd merely by shaking the sample together with the toluene—PPO—POPOP soln.

Fig 3 Comparison of Homogeneous Solution and Suspension Counting of Tagged HMX Samples

and 4% by wt Cab-O-Sil which can be added directly to the counting vial (Ref 8).

A direct comparison of homogeneous soln vs suspension counting is shown in Fig 3 for HMX samples tagged with Carbon-14 and with Tritium. Although completely insoluble in pure toluene, small amts of HMX can be dissolved in the toluene—PPO—POPOP scintillator containing dimethylsulfoxide in 25% by vol for homogeneous soln counting. The counting rates for increasing quantities of HMX—14C and HMX—3H are shown in 20mI vols of gel suspensions and homogeneous solns. The advantage in counting efficiency for the suspension systems in both cases is apparent. With the homogeneous solns, there is a marked decrease in counting efficiency with increasing concn because of quenching by the nitramino compd. The advantage of suspension over soln counting is even more obvious for the tritium-labeled expl. This is because the weaker light pulses produced by the action of the 3H betas in the scintillator are even more strongly affected by the quenching action of HMX molecules in soln.

For greater details on the techniques of LS counting in general, including the specialized nuclear instrumentation required and sample handling and preparation, see Refs 5, 6 & 7.

Written by S. HELF.
Refs: 1) C.G. White and S. Helf, Nucleonics 14, No 10 (1956), 46  
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Nuclear Tracers in Explosives

Chemistry

Radioactive tracer atoms have been used to study chemical reaction mechanisms in the production of TNT, RDX/HMX and NC. The results of these three independent investigations at PicArsn are summarized below:

Use of Carbon-14 to Study the Origin of Tetranitromethane (TeNMe) in TNT Manufacture.

In the production of TNT from the reaction between toluene and mixed acids (nitric/sulfuric), TeNMe forms in amounts between 0.2-0.4% of the total wt of TNT. This TeNMe has been held responsible for several expns which have occurred in TNT plants, causing fatal injuries to personnel and severe damage to facilities. These expns were attributed to the presence of TeNMe in the acid fume lines and the acid storage tanks. Mixts of TeNMe and readily oxidizable materials are known to form very powerful and sensitive expl mixts. Since TeNMe is also isolated from the nitration of Nitrobenzene (NB), the TeNMe formed in the nitration of toluene may arise from the oxidation of the aromatic ring and/or methyl group. In an effort to gain more information on the origin of TeNMe from TNT production, radioactive carbon-14 (14C) was used as a tracer to determine the extent to which each of the carbon atoms in the toluene skeleton of the various nitro-substituted isomers contributes to

TeNMe carbon (Refs 10 & 12)

The specifically labeled toluenes in the study were:

\[
\text{toluene-7-}^{14}\text{C} \\
\text{toluene-1-}^{14}\text{C} \\
\text{toluene-2,4,6,7-}^{14}\text{C} \\
\text{toluene-1,3,5-}^{14}\text{C}
\]

where the asterisk denotes the presence of the labeled carbon.

The contribution of the carbon atoms from the 1- and 7- positions to TeNMe carbon were obtained by determining the specific activity of the TeNMe isolated from the nitration of toluene-1-14C and toluene-7-14C, respectively. Similarly, by nitrating toluene-1,3,5-14C, it was possible to determine the 3- and 5-contributions, since the contribution of the 1-position could be subtracted and the 3- and 5-positions were considered to be equivalent. Finally, the contributions of the 2-, 4- and 6-positions were determined from the nitration of toluene-2,4,6,7-14C by subtracting the contribution of the 7-position. An approximate contribution for each of these positions (2-, 4- and 6-) was obtained by considering them to be equivalent.

The percentage of TeNMe carbon arising from each position in the toluene carbon skeleton is summarized as follows: 

\[
\begin{align*}
6.1 \\
8.3 & \quad 54.2 & \quad 8.3 \\
7.4 & \quad 7.4 & \quad 8.3 
\end{align*}
\]
The largest single contribution (54.2%) is from ring carbon-1 attached to the methyl group, and the bulk (94%) of the TeNMe formed is via oxidation of the aromatic ring. Additional 14C-tracer studies were conducted to determine the specific isomer participation for TeNMe formation. In the dinitration mixt there are six isomers present: 2,4-, 2,6-, 2,3-, 2,5-, 3,4- and 3,5-Dinitrotoluene (DNT). It was observed that 83% of the TeNMe formed from carbon-1 came from the DNT isomers derived from m-Nitrotoluene. The relative participation of DNT isomers for TeNMe formation is summarized in Table 1.

<table>
<thead>
<tr>
<th>Dinitrotoluene isomer</th>
<th>Isomer in Dinitrotoluene mixt, %</th>
<th>Participation rel to 2,4- and 2,6-Dinitrotoluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-</td>
<td>1.16</td>
<td>58.5</td>
</tr>
<tr>
<td>2,5-</td>
<td>0.56</td>
<td>93.6</td>
</tr>
<tr>
<td>3,4-</td>
<td>2.20</td>
<td>34.1</td>
</tr>
<tr>
<td>3,5-</td>
<td>0.08</td>
<td>793.0</td>
</tr>
<tr>
<td>2,4-</td>
<td>96.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The values in the last column of Table 1 represent the factors by which the TeNMe concen would increase over that of the total TeNMe arising from the nitration of 2,4- and 2,6-DNT if each of these isomers constituted 96% of the DNT mixt. Thus, the unsymmetrical Dinitro isomers of toluene, which constitute only 4% of the mixt contribute most heavily to the formation of TeNMe via oxidation of the aromatic ring.

From a chemical kinetic aspect, one can interpret these data such that the rate of nitration of the meta-DNT isomers is slower than the rate of nitration of the 2,4- and 2,6-DNT's. The values reported in the last column of Table 1 can thus be considered as a measure of the speed of nitration of the various isomers. That is, the larger the value of the participation in TeNMe formation, the slower the rate of nitration of the isomer to TNT. Therefore, according to these results, the nitration of 2,3-, 2,5-, and 3,4-DNT should be slower than that of 2,4- and 2,6-DNT; the nitration of 3,5-DNT should be even slower.

These data can also be explained from considerations of the profound effect that the groups attached to the aromatic ring have on both orientation and ease of introduction of the entering group. In the trinitration step, the orientation of the third nitro group is determined by one of the following effects: (a) Reinforcement of the directive influence of the methyl and two nitro groups. For example, in the nitration of 2,4-DNT, the methyl group favors substitution at the 6-position. The nitro groups also favor substitution at this position. The same situation exists in the nitration of 2,6-DNT. When total reinforcement occurs, the rate of nitration is rapid. (b) Entering nitro group is directed to the same position by the methyl group and one nitro group. This type of directive influence is observed in the nitration of 2,3-, 2,5- and 3,4-DNT. Since there is only partial reinforcement, the nitration proceeds at a slower rate and therefore more oxidation of the ring takes place. (c) No reinforcement of directive influence. This is observed in the nitration of 3,5-DNT. The nitration of this compd should proceed at a much slower rate, and attempts to nitrate it have been unsuccessful. Thus it will be subject to much oxidation and will contribute heavily to TeNMe formation.

The formation of TeNMe from the various DNT isomers was subsequently also studied at the Stanford Research Institute (Ref 17). The results agreed with those described above in that TeNMe was observed from all DNT isomers with the exception of the 2,4-DNT. No TeNMe was formed from the 2,4-isomers, whereas very small amounts were reported in the PicArsn study. However, the Stanford workers conjectured that the scale used in their study may have been too small to produce detectable quantities of TeNMe.

**Tracer Studies on the Nitrolysis of Hexamine to RDX and HMX.** The formation of RDX and/or HMX molecules from the nitration or nitrolysis of Hexamethylenetetramine (Hexamine) is a complex process and has been postulated to take place via two separate paths. One involves the selective cleavage of the Hexamine molecule to the appropriate cyclic nitramine (RDX, HMX or both) depending on the specific
nitrolysis conditions. The other assumes the complete degradation of the Hexamine molecule to methylene and amino or methyleneamino type fragments, followed by recombination of these fragments to a particular cyclic nitramine, or combination of both, again depending on the reaction conditions.

Detailed reviews of the chemistry of Hexamine and its nitrolysis to RDX, HMX and other related cyclic and linear polynitramines, including discussions of various postulated reaction mechanisms, are given by Smolin and Rapoport (Ref 9) and by Wright (Ref 15). Methods for the preparation of RDX are also described in Encycl 3, C611 to C615.

The following very brief discussion on synthesis of cyclic polynitramines is given merely to provide the historical background necessary to discuss the tracer studies:

The original practical method of RDX synthesis, as developed by Hale of PicArsn in 1925 (Ref 1), involves treatment of Hexamine with a large excess of abs nitric acid and results in 40% yield based on 2 moles of RDX from 1 mole of Hexamine. Ross and Schiessler (Ref 15), in 1940 at McGill University, succeeded in synthesizing the same compd from paraformaldehyde (p-CH₂O) and AN in Ac₂O in 35% yield based on p-CH₂O. (Subsequently, after WWII, this was found to be identical to the secret process of Eble, developed in Ger). The McGill workers postulated that, in their process, methylene nitramine (CH₂=N-NO₂) is formed as an intermediate, which then trimerizes to RDX. However, the existence of methylene nitramine has never been proven.

Werner Bachmann (Ref 2) of the University of Michigan, during WWII, conceived of a “combination process” in which the Hale nitrolysis of Hexamine would occur first, and the remaining methylene would be converted to RDX by the Rose-Schiessler route. Using three feed streams: Ac₂O, Hexamine in acetic acid, and AN in nitric acid, the Bachmann process results in an 80% yield of RDX (two moles from one of Hexamine), including a small amount of HMX. It should be noted that HMX is formed as a by-product in all three of these processes along with a variety of linear polynitramines. Subsequently, workers at the Holston Ordnance Works (now the Holston Defense Corp) (Ref 3) and at PicArsn (Ref 4) modified the original Bachmann conditions to yield a product more rich in HMX over RDX. At PicArsn, it was also demonstrated that by including a small quantity of p-CH₂O with the initial reactants, the yield of HMX/RDX mixt was increased to over 90% containing 85% HMX.

Although direct evidence in support of either the selective cleavage of Hexamine or the recondensation from small fragments mechanism is lacking, the former concept has been and still is preponderantly favored by the more classical researchers in this field. Smolin and Rapoport (Ref 9), in reviewing all of the work prior to 1959 on Hexamine nitrolysis with respect to isolation and identification of acetocmpd derivatives, conclude that “the evidence then is overwhelming with respect to the acetocmpds and all major and minor reaction products of Bachmann and Schiessler-Ross reactions that their synthesis proceeds by first the reformation of Hexamethylenetetramine followed by selective solvolytic (nitrolytic and acetolysis) cleavage rather than by synthesis of these products directly from fragments. The Schiessler-Ross reaction represents the second phase of the Bachmann reaction and constitutes a synthesis of Hexamethylenetetramine followed by a Hale type solvolyis.”

George F. Wright (Ref 15) of the University of Toronto, is equally adamant in his support of the selective cleavage route and is very explicit in illustrating his proposed mechanism (Fig 2).

Wright assumes that Hexamine is stabilized in soin as the dinitric acid salt. With strong nitric acid, as in the Hale process, nitrolysis at b,b′ leads to Compound A. Further nitrolysis of A at c results in RDX and dimethanolnitramine, O₂NN(CH₂OH)₂. A can also nitrolyze at d to give Compound B which upon loss of CH₂O can also result in RDX. It is noted, however, that neither A nor B has been isolated and that the existence of dimethanolnitramine is deduced by isolation of its diacetox analogue from the spent nitrolysis liquor. Under milder nitrolysis conditions, such as prevail in the Bachmann process, DPT is first formed from hexamine dinitrate via nitrolysis at a,a′. Upon further nitrolysis at f,f′, HMX is formed. Wright also explains the formation of linear polynitramines.
by the selective cleavage of A, B and DPT via different modes. In these various processes, where CH₂ groups are split off, they appear as CH₂O, which reform to Hexamine and thus “go thru the circuit” again. Wright designates this entire sequence of reaction schemes as “nitrolysis-resynthesis”. He makes it clear, however, that any resynthesis from fragments must go thru the reformation of Hexamine.

At PicArsn, the nitrolysis of Hexamine was studied using radioactive carbon-14 (Refs 7, 11) and stable nitrogen-15 (Ref 14) as tracers. Reaction conditions employed were a modification of the Bachmann Process (Ref 2) favoring the formation of HMX over RDX. In particular, the role of small amounts of added paraformaldehyde (p-CH₂O) in influencing higher yields of HMX, was examined. Briefly, a typical prep is: To a flask containing a slurry of paraformaldehyde, acetic acid and a trace of Ac₂O, the following reagents are added simultaneously at controlled rates over a 15-minute period: (a) a soln of Hexamine in gl acct acid, (b) Ac₂O, (c) a soln of AN in nitric acid. The reaction temp is maintained at 44 ± 1° throughout this procedure. The mixt is aged for 15 minutes and a second portion of Ac₂O and AN—nitric acid is added again over a 15-minute period. This reaction mixt is aged for another 60 minutes. Hot w is then added and the slurry is refluxed for 30 minutes. The HMX/RDX product is obtained by chilling and filtering this mixt. This procedure is diagrammatically illustrated in Fig 3.
(CH₂O)ₓ + 44 ± 1° reaction mixture 44 ± 1° DPT + 44 ± 1° 
HOAc 1st addn, 15 min at end of 1st 1st aging, 15 min spent nitro- 2nd addn, 15 min
Ac₂O Hexamine/HAc addition lyzing medium Ac₂O NH₄NO₃/HNO₃

trace Ac₂O NH₄NO₃/HNO₃

reaction mixture 44 ± 1° HMX/RDX + 110° H₂O reaction mixture at end of 2nd spent nitrolyzing medium 2nd aging, 60 min H₂O reflux, 30 min Filter

Fig 3 Flow Diagram for the Nitrolysis of Hexamine

From this process, the yield of HMX/RDX is approx 90% of theory (based on Hexamine molecule), and 85% of this mix is HMX.

The tracer expts conducted to study the mechanism of nitrolysis and product formation in the above process are briefly outlined in Table 2.

<table>
<thead>
<tr>
<th>Tagged Species</th>
<th>Products Isolated &amp; Assayed for Tagged Atom Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamine-¹⁴C</td>
<td>HMX, RDX</td>
</tr>
<tr>
<td>Paraformaldehyde-¹⁴C</td>
<td>HMX, RDX</td>
</tr>
<tr>
<td>Paraformaldehyde-¹⁴C</td>
<td>DPT</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>HMX, RDX</td>
</tr>
</tbody>
</table>

In the carbon-14 expts, HMX/RDX product was isolated qualitatively, separated into its components, and each component assayed for carbon-14 beta radioactivity using a liquid scintillation counting technique (Ref 11). DPT-¹⁴C was isolated as an intermediate product from the reaction mixture and similarly radioassayed. For the nitrogen-15 tagged AN expts, HMX and RDX were assayed mass spectrometrically for ¹⁵N/¹⁴N ratios from which atom %¹⁵N contents were calc'd. In the course of these expts, each tagged species was added initially and also at subsequent stages of the reaction process. The important observations and results are summarized as:

1. During the first stage in the addition of reactants and aging, all of the original Hexamine and p-CH₂O is consumed and DPT is the major product isolated. The quantity of DPT isolated is approx doubled when p-CH₂O is included.

In the formation of DPT, a complete equili-
(9) In the absence of p-CH$_2$O, HMX and RDX are derived mainly from Hexamine nitrogen with about 5% of the RDX derived from AN. In the presence of p-CH$_2$O, 7% of the HMX and 40% of the RDX are formed from AN.

The interpretation drawn from the above results is that in the first reaction stage, Hexamine degrades non-selectively and completely to methylene containing fragments which then recondense to form DPT. Similarly, in the second stage, DPT also degrades non-selectively, with all –CH$_2$ groups chemically equivalent, to reform the insoluble cyclic nitroamines which remain stable in the spent nitrolysis medium. Therefore, the relative ratio of HMX to RDX is not controlled by the selective cleavage of a large molecule but is rather influenced by the particular conditions controlling the recombination of a common methylene-containing fragment such as HOCH$_2$NHNO$_2$ or

[-CH$_2$N–NO$_2$]. The authors postulate that the addition of p-CH$_2$O increases the concn of methylene-containing fragments which exist in the precursors to HMX/RDX, and thus accounts for the small increase in yield of these products.

The path of amino nitrogens in this process is more difficult to deduce from the results of the tracer expts because the rate of exchange of amino nitrogens among the various reactant species is faster than the rate of reaction. Nevertheless, it is clear that the C–N bonds in the un-nitrated amino group, –CH$_2$–NH–CH$_2$–, are highly labile in the nitrolysis medium and are readily subject to rupture; on the other hand, once formed, the nitramino group, –CH$_2$–N–NO$_2$, is completely stable, and the corresponding C–N and N–N bonds are neither subject to exchange nor are they readily degraded in the spent nitrolysis medium.

Although the results of these tracer studies with carbon-14 and nitrogen-15 were published in 1960 and 1965, respectively, there has been no stampede, on the part of polycyclonitramine chemists to get on board the “synthesis from fragments” bandwagon. On the contrary, in reviewing these tracer studies, Wright (Ref 15) actually concludes that these “results are not contradictory to the nitrolysis-resynthesis postulation” involving the reformation of Hexamine. An apparent weakness, however, in Wright’s thesis, as illustrated in Fig 2, is the assumption that HMX can only be formed thru the precursor DPT. The PicArsn studies (Refs 7, 11) did substantiate the formation of DPT as the major intermediate under Bachmann reaction conditions. However, HMX has been identified or isolated as an impurity or minor product in almost every synthetic route leading to RDX, including conditions where DPT is not necessarily formed.

In addition to the Ross-Schiessler process, utilizing p-CH$_2$O and AN, the synthesis of RDX/IMX mixts has also been reported starting with other small molecules (Ref 7), namely, methylamine nitrate; methylenediamine dinitrate; and nitramine (NH$_2$NO$_2$) in combination with CH$_2$O. In these reactions, the intermediate formation of Hexamine or a cyclic analog, is not necessarily established.

Bell and Dunstan (Ref 16) have reported that the addition of methylenedinitramine to Hexamine nitrolysis mixts, aged at 0° for 5 and 120 minutes, gave RDX in yields of 120 and 106%, respectively, compared with 52 and 83% in the absence of the dinitramine. However, rather than supporting a synthesis from small molecules, the authors contend that these results substantiate the existence of a postulated bis(nitroxyethyl) aminomethyl precursor of RDX, namely:

\[
\begin{align*}
\text{O}_2\text{NN} & \quad \text{CH}_2 \\
\text{H}_2 & \quad \text{N} \quad \text{CH}_2 \\
\text{O}_2\text{NOH}_2 & \quad \text{CNCH}_2\text{ONO}_2
\end{align*}
\]

It should be noted that this intermediate is the dinitroxy derivative of Compound A, postulated as the precursor for RDX by Wright according to Fig 2.

The synthesis of RDX via the Triazine Process (Ref 13) involves the condensation of formaldehyde with acetonitrile followed by nitration:

\[
3\text{CH}_2\text{O} + 3\text{CH}_3\text{CN} \rightarrow [\text{CH}_2\text{NCOCH}_3]_3 + 3\text{HNO}_3
\]

RDX + 3CH$_3$COOH

Although the yield of RDX is high, the economic advantage of the Thatcher Process over Hexamine nitrolysis is yet to be demonstrated (Ref 19).
RDX has also been prep'd in high yields by the nitration of the condensation product of CH₂O and potassium sulfamate (Wolfram Process) (Ref 15):

\[
\text{CH}_2\text{O} + \text{NH}_2\text{SO}_3\text{K} \rightarrow \text{KO}_3\text{SN}^\\beta\text{CH}_2\text{NSO}_3\text{K}
\]

\[\text{HNO}_3 \rightarrow \text{RDX} \]

liq SO₃ or P₂O₅

This method is not economical because of the high cost of the starting materials.

Solomon, of the Illinois Institute of Technology Research Institute (IITRI), has reported the synthesis of HMX from the condensation of straight chained nitramines, bis(hydroxy-methyl) methylene dinitramine and methylene dinitramine. However, details of this work were not available as of this writing.

Thyagarajan and Majumdar (Ref 18) have studied the condensations of urethanes with formaldehyde under various expit conditions and accomplished the selective synthesis of either six-membered 1,3,5-triazines or eight-membered 1,3,5,7-tetrazocines. These are non-nitrated analogs of RDX and HMX respectively. Their results are summarized in Fig 4.

Condensation of methyl urethane, H₂NCOOCH₃, with CH₂O gives rise to the methylene diurethane (III) and this compd, under different specific conditions of refluxing, results in the various specific linear (IV & V) and cyclic products (I & II) as shown. The observations of relevance here are that the various products, both linear and cyclic, are interconvertible under acid catalysis including I into II and conversely. The authors have thus shown that “the condensation of urethanes with formaldehyde under acid catalysis affords a variety of products, depending upon the reaction temp and length of reaction time. Products of such condensation are capable of reversal to their constituent components and resynthesis to simple or complex products”. In the opinion of this writer, the analogy of the observations with these systems with those observed from the tracer expts with Hexamine nitrolysis is striking.

Fig 4 Condensation Products of Urethane with Formaldehyde

In conclusion, there appears to be some supporting evidence, other than these tracer studies, that the synthesis of HMX and RDX molecules can be accomplished thru a build-up from single methylene-containing species or other small molecules, and that this route can also take place via a total degradation and resynthesis from molecules such as Hexamine. However, the development of an economical process for the large scale production of these expit nitramines, in particular HMX, via a method precluding the use of Hexamine, is yet to be accomplished.

Use of Sulfur-35 to Characterize the Sulfate Content in Nitrocellulose (NC). Military grades of NC are prepared by nitrating a suitable grade of cellulose, either cotton linters or wood pulp, with a mixt of nitric and sulfuric acids. After nitrination, the great bulk of the spent acid is removed by centrifuging, and the NC is drowned in w. In the USA, a long stabilization treatment follows, consisting of (a) three preliminary
boils in acidulated w, (b) beating to a desired fineness, (c) four additional boils, and (d) several cold w washes. This prolonged treatment, which is considered necessary to obtain NC with a satisfactory degree of stability, has been developed empirically (See Vol 2, C107). Numerous expn studies have been made to explain the need for the extended stabilization treatment and, if possible, to shorten it. Analytical data have been obtained which show that the pre-stabilized, ie, freshly prep and drowned NC contains appreciable quantities of sulfate (up to about 1%). Instability of NC has been generally attributed to the presence of this sulfate content, and the prolonged boiling and beating process is considered by many workers as necessary to remove this impurity. The literature contains many reports of investigations dealing with the nature of the sulfate content in NC and its effect on the stability of the product (Ref 5). However, the subject is replete with diverse and conflicting statements. The different theories of the stabilization of NC, particularly as related to the role of the sulfate impurity, can be summarized as follows:

Theory A. Unstabilized NC contains appreciable quantities of chemically combined sulfur in the form of sulfate esters plus occluded free sulfuric acid. The primary step in the stabilization is hydrolysis of the sulfuric esters which is promoted by boiling the NC in an acid medium. The esters, present as the half ester, RO\textsubscript{2}SO\textsubscript{3}OH, and to some extent as the full ester, RO\textsubscript{2}SO\textsubscript{4}O\textsubscript{2}, (where R = NC residue), are considered to be much more easily hydrolyzed than their metallic salts, RO\textsubscript{2}SO\textsubscript{4}O\textsubscript{2}, which are believed to form in the presence of alkaline or alkaline earth solns.

Theory B. All NC before stabilization, contains a certain amount of residual nitratin acids consisting of both nitric and sulfuric acids, but mostly the latter. The occluded sulfuric acid is trapped in the fine structure of the NC fibers and renders the products less stable, especially at elevated temps. The amount of sulfate esters present, if any, is small in quantity and easily hydrolyzed by merely washing the fibers with cold w. Boiling the NC in a w or acid medium enhances the diffusion of sulfuric acid from the inner structure of the fibers and facilitates removal of the acid by subsequent washing.

Theory C. Instability of NC is due to the presence of three types of impurity. These are: occluded free sulfuric acid, sulfuric hemiesters and full esters, and nitrated degradation products of cellulose. The hemiester content is less in more highly nitrated cellulose, whereas the free sulfuric acid content is greater. The acid boil stabilization procedure removes all three types of impurity.

Theory D. The presence of small quantities of sulfate, either as combined or free acid which is readily removed, does not greatly affect the stability of the NC. The real cause of instability is the presence in more intimate association with the NC, of other compds which cannot be removed by exhaustive washings. These compds which are acidic in character and exist in small quantities, are formed during the nitration of the cellulose. They can be removed only by prolonged boiling in either w or alc. The presence of acid or salt solns does not increase the ease of stabilization during boiling.

The nature and amount of sulfate content present in NC and the mechanism for its removal during the stabilization process was investigated at PicArsin using the radioactive tracer, sulfur-35 (Ref 5). Through the use of this radionuclide, a rapid and sensitive radiometric method for sulfate analysis in NC samples was developed by tagging the sulfuric acid in the nitrating mixed acid. The magnitude of the beta activity of the sulfur-35 in the sample is directly proportional to the total sulfate content present, either as free sulfuric acid or some chemically combined state. With this tracer technique a large number of sulfate determinations are easily performed at one time. Samples of NC with as little as 0.004% sulfate were accurately analyzed by this method (Ref 6).

Determination of the nature of the sulfate content was attempted by following the concn of this impurity in two ways: (1) during the course of laboratory simulated industrial stabilization procedures, and (2) from successive dissolutions of unstabilized NC samples in various solvents and subsequent repptn from non-solvents. This approach was based on the premise that free occluded sulfuric acid would be released from the fibers by the soln-pptn treatment, whereas chemically combined sulfate would remain unaffected. The full details of the various expts can be found in Ref 5; some typical results are shown in Table 3 for four samples of NC of different nitrogen content.
Table 3
Comparison of Sulfate Removal in Samples of Nitrocellulose by Acid Boil and Precipitation Treatments

<table>
<thead>
<tr>
<th>Percent Sulfate of Nitrocellulose Samples:</th>
<th>After Treatment by THF-Benzene Precipitations</th>
<th>After Treatment by 56-hr Acid Boil plus treatment by THF-Benzene Precipitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Nitrogen</td>
<td>Prior to Treatment</td>
<td>After Treatment</td>
</tr>
<tr>
<td>13.09</td>
<td>0.72</td>
<td>0.05</td>
</tr>
<tr>
<td>13.37</td>
<td>0.80</td>
<td>0.05</td>
</tr>
<tr>
<td>13.13</td>
<td>0.97</td>
<td>0.09</td>
</tr>
<tr>
<td>13.35</td>
<td>0.84</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The important observation from the data in Table 3 is that NC samples subjected to acid boil followed by tetrahydrofuran (THF)-benzene treatment yielded essentially the same sulfate contents as samples subjected to THF-benzene treatment alone. From this the authors interpret "that sulfate contents from THF-benzene treatments actually represent absolute values of the difficult-to-remove sulfate which may very well be true sulfate ester". It is also tentatively concluded that approximately 90% of the original sulfate content in unstabilized NC is readily removable sulfuric acid with the remainder the "more difficult-to-remove" sulfate ester. Dilute acid boil treatment of NC for 56 hours does not eliminate all of the free sulfuric acid and leaves the "difficult-to-remove" sulfate practically unchanged.

In a later investigation, radioactive sulfuric acid was also used to study the removal of occluded acid from freshly nitrated cellulose by cold saline leaching (Ref 8). It was observed that extraction with Na sulfate soln causes a greater release of acidity than extraction with distilled w. Of the total acidity released, the bulk is sulfuric acid and the remainder, nitric acid. The amount of acidity released by saline leaching is inversely related to the nitrogen content of the NC, that is, less acid is extracted when the NC has a higher nitrogen content. The same reference also describes the evaluation of a cold saline leach in combination with short aq boils to produce a stable NC from cotton linters. The 100° vacuum stability test showed that a combination of a 4-hour cold saline leach and a 10-hour w boil, before the standard beating and poaching operation, resulted in a pyrocellulose (12.6% N) comparable in stability to a sample boiled for 40 hours. However, the substitution of a saline leach for boiling time appeared to have no advantage for high grade (13.45% N) NC. The use of saline leaches for the stabilization of NC was judged to be of no particular advantage.

Written by S. Helf

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8) R.N. Shelley & S. Helf, "Use of Saline Leaches to Stabilize Nitrocellulose", PATR 2550 (1958)
11) T.C. Castorina et al, JACS 82 (1960), 1617
12) F.S. Holahan et al, JACS 84 (1962), 756
13) D.W. Thatcher,
Nudets. A US nuclear detonation warning system. A matrix of seismic sensors spread throughout the USA intended to estimate the point of impact and power of nuclear-detonated nuclear warheads. 


Nuevo Anagón. A Spanish Ammonal containing AN 70, Al-Zn alloy 10% & charcoal 10%. See also Vol 1, A292-L

Ref: A. Pérez Aria (1945), 247

Nuodex. See under Laminac 4116 in Vol 7, L3-L

Nutation. The axis of a spin-stabilized projectile in flight is subject to spasmodic small conical vibrations, called nutation, which should not be confused with yaw (qv) or precession (qv). The instant a spinning projectile leaves a gun, the turbulence produced by the release of propellant gases causes nutations to occur. Their amplitude is usually small, and, in the case of concentric fast spinning projectiles, they disappear due to the action of equal and opposite centrifugal forces. If the projectile spin is insufficient, the amplitude of the nutations increases, soon causing the projectile to tumble in flight.


NX (Explosif) (Nitrate d’ammoniaque–Xylite). A fr military expl consisting of AN 70 & Tri-nitroxylene 30%, used as a bursting charge in projectiles.


Nylon, Aminoethyl. See under Aminoethyl nylon (AEN) and Its Perchlorate (AENP) in Vol 1, A205-L

Nyeastine. A Dynamite patented in 1876 by Fahneljelm containing NG 45–48, charcoal 15–35, Na or K nitrate (or chlorate) 5–25, & Na carbonate 5% max

Ref: Daniel (1902), 586

Nysol. An expl prep by nitrating a sol of naphthalene in xylene, and used as an ingredient of low-freezing Dynamites

Ref: Bebie (1943), 112
O, Explosifs du type. Fr designation for Cheddites. See Vol 2, C155-L ff

Oakley Quarry Powder. A blasting expl consisting of AN and Tetryl
Refs: 1) Marshall, Dict (1920), 69 2) Thorpe’s Dict (1940), 487

Oaklites. Brit expls of the “Carbonite” type (see Vol 2, C61-R) contg NG 24.0–26.0, NC 0.5–1.5, K nitrate 32.5–35.5, woodmeal 33.5–36.5 & Mg carbonate 0.5%
Ref: Naoum, NG (1928), 402

Qare Powders. Expls manufd in 1898 by the Cotton Powder Co, Ltd, of Faversham (Kent), Engl. They originally contained, as the main ingredients, Chile saltpeter (Na nitrate) and Dinitrobenzene, but later the latter ingredient was replaced by TNT
Ref: Daniel (1902), 587

Oarite. An expl patented by Trench in 1891 contg NG 20, NC 10, Dinitrobenzene 10, K and Ba nitrates 60%
Refs: 1) Daniel (1902), 587 2) Giua, Trattato VI (1) (1959), 386

Oat Hulls, Nitrate. Proposed as an ingredient of expls in combination with such oxidizers as AN, Na nitrate, etc: Nitrate balsam pulp or bagasse (see Vol 2, B4-L) could also be used
Ref: W.deC. Crater, USP 2096089 (1937) & CA 32, 357 (1938)

Obermüller’s Test. One of the tests for detg the stability of NC based on heating the sample in a vacuum and measuring the evolved gas by means of a Hg monometer. Prior to Obermüller’s invention (1904), the concept of measuring the gas press was used by Abel, Hesse and Mitsch, but their apps were not as convenient to use as that of Obermüller. The method was soon adopted in Germany and Spain, and was used for many years. It was later modified by Wilcox (Refs 3 & 4), Pleus (Ref 5) and Lenze (Ref 6)

It should be noted that nearly simultaneously with Obermüller, A. Dupré invented a very similar method (Ref 8, p 245), and that Taliani’s method [GazzChimItal 51, I, 184 (1921)] can be considered an improvement over that of Obermüller

Following is a brief description of the method. It is simpler than that of Bergmann and Junk (see Vol 2, B102-R), which was invented earlier and used by the Ger Govt since 1898 Procedure. A weighed quantity (1 to 2g) of NC to be tested is placed in a 12ml test tube, with a small glass rod with a flattened end resting on the surface of the NC to prevent it from being ejected upward on the application of vacuum. By means of a ground-glass connection, the top of the test tube is connected to a retort-shaped tube, which in turn is connected to a manometer. After evacuation of the air, the test tube is placed in a bath previously adjusted to a standard temp (135° or 140°), which is maintained through the duration of the test. The NC begins to decom immediately and yield gaseous products, and the rate of decompn is measured by the increase in press, this rate being greater for NC of poor stability

Working at a standard temp of 140° with a tube, with its connections, having a vol of 37ml, Obermüller found that 1g of stable NC did not cause a greater press increase than 100mm of Hg in one hour. Tests conducted by Wilcox with stabilized US mil NC’s indicated that in most cases the press developed in 60 minutes was about 100mm of Hg (Ref 3, p 274)

The rate of decompn, calc’d from data obtained using Obermüller’s test, agrees fairly well with those calc’d using Sapochnikoff’s formula (Refs 2 & 3, p 2801)
Refs: 1) P. Obermüller, JSCI 24, 347 (1905)
2) A. Sapochnikoff, JRussPhysChemSoc 36, 1186 (1906) 3) O.W. Wilcox, JACS 30, 271 (1908)
O'Brien Explosives. A series of patents were issued to J.F. O'Brien of Chicago, Ill, USA between 1913 and 1915 for new commercial expls. Typical formulations included K chlorate 30, Nitrostarch 10, Si dioxide 55, & crude petroleum with coal dust 5ps (Ref 1); K chlorate 87, naphthalene 6.5, asphalt 6.5, crude oil distillate 1.5 & Si dioxide 44ps (Ref 2); K chlorate with Na nitrate 60, liq TNT 15 & sawdust 25ps (Ref 3); and Amm perchlorate 20–65, Na nitrate 55, liq DNT 10–15, sawdust 14–23 & free C 1–3.5ps (Ref 4)

Refs: 1) J.F. O'Brien, USP 1070836 & USP 1070837 (1913) & CA 7, 3416 (1913)
2) Ibid, USP 1071949 (1913) & CA 7, 3542 (1913) 3) Ibid, USP 1073279 (1913) & CA 7, 3665 (1913) 4) Ibid, USP 1132873 (1915); Calver (1938), 685

Obscuring Power of White Smokes. The total obscuring power, TOP, of a white smoke agent used for screening purposes, is obtained by multiplying the product of volume, in cubic ft or smoke produced per lb of material, and the reciprocal of the smoke layer, in ft, necessary to obscure the filament of a 40-watt Mazda lamp. The TOP for some white smoke agents, at low altitudes where atm constituents are plentiful, is given in Table 1

<table>
<thead>
<tr>
<th>Chemical</th>
<th>TOP, ft²/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>White Phosphorus</td>
<td>4600</td>
</tr>
<tr>
<td>TiCl₄ + NH₃</td>
<td>3030</td>
</tr>
<tr>
<td>SO₃</td>
<td>3000</td>
</tr>
<tr>
<td>FS</td>
<td>2550</td>
</tr>
<tr>
<td>HCl + NH₃</td>
<td>2500</td>
</tr>
<tr>
<td>HC Mixture*</td>
<td>2100</td>
</tr>
<tr>
<td>SiCl₄ + NH₃</td>
<td>1960</td>
</tr>
<tr>
<td>FM*</td>
<td>1900</td>
</tr>
<tr>
<td>Oleum</td>
<td>1890</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>1860</td>
</tr>
<tr>
<td>PCl₃ + NH₃</td>
<td>1600</td>
</tr>
<tr>
<td>PCl₃ + NH₃</td>
<td>1800</td>
</tr>
<tr>
<td>HCISO₃ + NH₃</td>
<td>1600</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>1500</td>
</tr>
<tr>
<td>HCISO₃</td>
<td>1400</td>
</tr>
<tr>
<td>BM Mixture*</td>
<td>1400</td>
</tr>
<tr>
<td>BergerMixture</td>
<td>1250</td>
</tr>
<tr>
<td>FM + 1,2-Dichloroethane</td>
<td>1235</td>
</tr>
<tr>
<td>SO₂Cl₂</td>
<td>1200</td>
</tr>
<tr>
<td>Cl₂ + NH₃</td>
<td>750</td>
</tr>
<tr>
<td>AsCl₃</td>
<td>460</td>
</tr>
<tr>
<td>Type-S Mixture*</td>
<td>460</td>
</tr>
<tr>
<td>Crude Oil</td>
<td>200</td>
</tr>
</tbody>
</table>

*FS-chlorosulfonic acid & sulfur trioxide
HC Mixture-hexachloroethane, zinc, inorg perchlorate & amm chloride
FM-titanium tetrachloride
BM Mixture-zinc, carbon tetrachloride, sodium chloride, amm chloride & magnesium carbonate
Berger Mixture-zinc, carbon tetrachloride, zinc oxide & kieselguhr
Type-S Mixture-sulfur, inorg nitrate & charcoal

The so-called "standard smoke" is a smoke of such a density that a 25-candlepower light is just invisible when observed thru a layer 100 ft thick. A comparison of some white smoke agents at low altitude, where atm constituents are plentiful, in terms of the amount of smoke agent required to produce 1000 cubic ft of standard smoke, is given in Table 2
Table 2
AMOUNT OF SMOKE AGENTS REQUIRED TO PRODUCE 1,000 CUBIC FEET OF STANDARD SMOKE

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount Required, oz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>0.060</td>
</tr>
<tr>
<td>FM + NH₃</td>
<td>0.090</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.094</td>
</tr>
<tr>
<td>FS</td>
<td>0.110</td>
</tr>
<tr>
<td>HC Mixture</td>
<td>0.120</td>
</tr>
<tr>
<td>FM</td>
<td>0.150</td>
</tr>
<tr>
<td>Oleum</td>
<td>0.151</td>
</tr>
<tr>
<td>Crude Oil</td>
<td>2.000</td>
</tr>
</tbody>
</table>

All of the TOP and standard smoke measurements are made at low altitude, where atm constituents available for reaction with the primary smoke particles are plentiful. The importance of atm constituents is illustrated in Table 3 where the number of grams of smoke formed per gram of smoke agent used is tabulated.

Table 3
AMOUNT OF SMOKE PRODUCED PER UNIT WEIGHT OF SMOKE AGENT AT 75% RELATIVE HUMIDITY

<table>
<thead>
<tr>
<th>Agent</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fog Oil</td>
<td>1.0 (does not produce aqueous solution)</td>
</tr>
<tr>
<td>Zinc Chloride</td>
<td>2.5 (water vapor absorbed)</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>3.1 (water vapor absorbed)</td>
</tr>
<tr>
<td>Aluminum Chloride</td>
<td>5.0 (water vapor absorbed)</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>7.11</td>
</tr>
</tbody>
</table>

It is evident, for the agents compared, that white P yields the greatest weight of as soln in equil with air at 75% RH per unit-weight of the smoke agent. The ratio for fog oil is unity (1.0) since the fog oil is not hygroscopic and only the agent is available to form the smoke particles. The values do not take into account ingredients which remain behind as residues or otherwise contribute little to the obscuring power. The absolute values will vary with the RH, but change very little with air temp at any one value of the RH. Also, the relative results are not changed. It is important to note that these measurements chiefly concern the obscuring or screening power of the smoke and no consideration is given to other factors which might be important for a signal smoke, tracking aid, or tracking and acquisition smoke.


Obstruction Test for Smokeless Powders. See under Methyl Violet Tests in this Vol

Obtrurate. To stop or close an opening so as to prevent escape of gas. To seal, as with delay elements
Ref: OrdTechTerm (1962), 207-R

Obstructed, or Percussion Type Primer. A type of primer which consists of a cup into which the primer charge is loaded, and an anvil which is pressed into the open end of the cup, its point extending slightly into the mixt. A paper disc is placed over the mixt before assembly to assist in sealing. A primer of this type is usually pressed into an amm component and fired by hitting the bottom of the cup with a firing pin, which forces the mixt against the anvil. Since the cup is not pierced, obturation (sealing) is obtained after the primer is fired because the primer as a whole is pressed into its containing cavity. The primer cups are constructed of ductile metals, commonly brass, in order to avoid rupture by the firing pin

Obturation. A process that seals the breech of a gun and prevents the escape of propellent gases at the time of firing. In all modern firearms, light and medium artillery, it is effected by the momentary expansion of the brass or copper cartridge case.

In separate-loading amm, obturation is achieved by a special device, called an Obturator (qv)
The term obturation is also applied to the sealing of the chamber in which the delay element of an expi train is located. Obturated delay elements are so constructed as to retain all gases emitted by the initiator and the delay element until the relay or other base charge explds. Advantages of obturated delays include the inherent independence of these sealed units from effects of press or humidity of the ambient atm, and the absence of fumes that might have harmful effects on other components of the system. Obturation also helps in the design of short delays, because the resulting increase in press increases the burning rate


Obturator. An assembly of steel spindle, mushroom head, obturator rings, and a gas-check or obturator pad of tough plastic material used as a seal to prevent the escape of propilt gas thru the breechblock of guns using separate-loading ammo, and therefore not having the obturation provided by a cartridge case

A device incorporated in a projectile to make the tube of a weapon gas-tight, preventing escape of gas until the projectile has left the muzzle

Ref: OrdTechTerm (1962), 207-R

Obturator Pad. Pad of tough plastic material, forming part of an Obturator (qv)

Ref: OrdTechTerm (1962), 207-R

Obturator Rings. Accurately machined and fitted rings forming part of an Obturator (qv)

Ref: OrdTechTerm (1962), 207-R

Obturator Spindle. Part of the breechblock assembly of a gun which fires separate-loading ammo. It extends thru the breechblock and holds in position the various parts of the Obturator (qv), while permitting the breechblock independent rotation around these parts

Ref: OrdTechTerm (1962), 207-R

Obus (Fr). Artillery shell
Obus à balles (Fr). Shrapnel
Obus à coiffe (Fr). Shell with armor-piercing cap
Obus à culot tronconique (Fr). Boat-tailed shell
Obus à étoiles (Fr). Star shell
Obus à fragmentation (Fr). Fragmentation shell
Obus à gaz (Fr). Gas shell
Obus à ogive trempée (Fr). Shell with hardened cap
Obus à segments (Fr). Segment shell
Obus bivalente (Fr). HE shell with chemical filler
Obus brisant (Fr). HE time shell
Obus d'emploi particulier (Fr). Chemical shell
Obus D en forte aciérie (Fr). Cast steel shell
Obus de réglage (Fr). Special shell for adjustment of fire
Obus de rupture (Fr). Armor-piercing shell
Obus d'exercice (Fr). Dummy projectile
Obus éclatant (Fr). Illuminating shell
Obus explosif (Fr). HE shell
Obus fumigène (Fr). Smoke shell
Obus fusant (Fr). Time shell
Obusier (Fr). Howitzer
Obusier de siège (Fr). Siege howitzer
Obusier sur bât (Fr). Pack howitzer
Obus incendiare (Fr). Incendiary shell
Obus non éclaté (Fr). Dud
Obus perforant (Fr). Armor-piercing shell
Obus plein (Fr). Shot, solid shell
Obus toxique (Fr). Gas projectile, gas shell
Obus traceur (Fr). Tracer shell


Occupational Diseases and Hazards in Explosives and Ammunition Plants. See under Industrial Hygiene in Vol 7, I93-R

OC, Explosifs du type. Fr designation for Ched-dites. See Vol 2, C155-L ff

e-Chlorobenzylmalononitrile (CS).

\[ \text{CIC}_6\text{H}_4\text{H}(\text{CN})_2 \]

mw 188.5, white cryst powd, mp 93–95°, bp 310–315°, bulk d 10–20 lbs/cu ft, pepperlike odor. CS has a min purity of 96%; is insol in w and alc, sol in methylene chloride

CS is a tear agent used for training and riot
control (see Chemical Agents or Chemical Warfare Agents in Vol 2, C165-RF)

Median lethal dosage. 25000mg-min/m³ for resting men

Median incapacitating dosage. 10 to 20mg-min/m³

Rate of detoxification. Quite rapid, incapacitating dosages lose their effects in 5 to 10 minutes

Skin and eye toxicity. Highly irritating but not toxic

Rate of action. Very rapid

Physiological effects. CS produces immediate effects even in low concns. The median effective concn for respiratory effects is 12 to 20mg/m³; concn for eye effects is 1 to 5mg/m³. The onset of incapacitation is 20 to 60 seconds and the duration of effects is 5 to 10 minutes after the affected individual is removed to fresh air. During this time affected individuals are incapable of effective concerted action. The physiological effects include extreme burning of the eyes accompanied by copious flow of tears; coughing, difficulty in breathing, and chest tightness; involuntary closing of the eyes; stinging sensation of moist skin; running nose; and dizziness or swimming of the head. Heavy concns will cause nausea and vomiting in addition to the above effects

Protection required. Protection is provided by the protective mask and ordinary field clothing secured at the neck, wrist, and ankles. Personnel handling CS should wear rubber gloves for additional protection

Decontaminants. Area decontamination is not required as CS has a short duration of effectiveness. Personnel exposed to CS may shower as necessary; however, when CS dust or particles are on the skin, showering should be delayed for 6 hours to prevent stinging and reddening of the skin. Individuals affected by CS should move to fresh air, face the wind, and remain well spaced; and should not rub their eyes. To remove accidental gross contamination, personnel should remove clothing and immediately flush body with copious amts of water to remove most of the agent; apply 5% Na bisulfitie soln to remove remainder (except in or around eyes); and then rinse body

Munitions suitable for use. The pure crystal form (identified by symbol CS) is used as filling for burning-type grenades and capsules. A mixt of 95% of the crys agent and 5% of silica gel aero-gel (identified by symbol CS1) is used as filling for bursting-type grenades and in all bulk irritant agent dispersers


Ochsé's Cartridges. These cartridges, patented in Fr in 1893–94, were made of 2.5mm thick steel, 3cm in diameter and 18cm long, and could withstand a press up to 1200 atms. Prior to use, they were filled with Na hydroxide soln, and then tightly closed. An electric current of 0.85 to 1.0 amp and 8–10 volts was then passed thru the soln until it completely decompd into H₂ and O₂. After placing such "charged" cartridges into the bore-holes of mines, they were connected to a source of electrical current. The electric sparks, produced by the current, caused an expln inside the cartridge. The effect produced by each steel tube was equivalent in strength to a 150g cartridge of an AN expl, such as Westphalite (qv) or Dahmenite (see Vol 3, D1-R)

Tests conducted at the end of the last century at Mont-Cenis, Fr, and Westphalia, Ger, indicated that the use of Ochsé's cartridges was uneconomical and dangerous

Ref: Daniel (1902), 588

Octamethylolelocyclohexanediol,
HOHC[C(CH₂OH)₂]₆CHOH, mw 356.36, can be prepd by reduction of the corresponding "dienes". Octamethylolelocyclohexanediol,
OC[C(CH₂OH)₂]₆CO, mw 352.33, can be prepd by condensation of the corresponding cyclic ketone with aldehyde

Both of these compds yield expls on nitration. It is claimed that these exps have a high detonation velocity, can be poured at temps below 100°, and are stable when stored at 50°

The same investigators proposed the use of nitrates of other cyclic keto-alcohols, such as tetramethylolelolelocyclohexanone, tetramethylolelocyclopentanone, etc, as expls. All of these alcohols can be prepd by condensing cyclic ketones with formaldehyde in the presence of alkalies or al-
kaline earths
Refs: 1) W. Friederich & K. Flick, GerP 509118 (1929) & CA 25, 819 (1931) 2) W. Friederich, BritP 345859 (1929) & CA 26, 2058 (1932)

Octanitrocellulose. [also called Dinitrocellulose, C₅H₉O₃(NO₂)₂, or Tetrinitrocellulose, C₁₂H₁₆O₆(NO₂)₄]; C₂₄H₂₄O₁₂(NO₂)₈; mw 1008.56; N 11.11%; d 1.653 g/cc; 178 ml of NO evolved per 1 g sample; wh amorph mass
Sol in abs alc, gl acet acid, acet, eth/alc mixts, ethyl acet, NG, etc. Can be prep by the nitration of cellulose with nitric acid in the presence of equal amts of sulfuric and phosphoric acids
Octa- and hexanitrocellulose are the principal ingredients of Collodion (see Vol 3, C394-R), with the former being within the N range of Collodion Cotton (see Vol 2, C103-R)

Octanitroethylenediphényldiamine. See Ditetryl or Biteteryl in Vol 5, D1513-L.

Octazatrienes or Octazones. Derivatives of HN:NH:N=NH:N=N, some of which are expl. They were described by their discoverers, Wohl and Schiff (Ref 3), “as standing on the very edge of existence”
A typical derivative is 3,6-Diphenyl-1,8-bis-[4-bromphenyl]-octazatriene-(1,4,7) or N,N'-Bis[4-brombenzoldiazia]-N,N'-diphenyltetrazione. C₆H₄Br:N=N(C₆H₄)₂:N=N(C₆H₄)₂:N=N:C₆H₄Br, pale yel substance, mp 60°C. Can be prep by treating a cold ethereal soln of 3-phenyl-1-[4-bromphenyl]-tetrazene-(1) with a 1% soln of K permanganate (Ref 1). It is an expl
Refs: 1) Bel 16, 756 2) F. Wohl & H. Schiff, Ber 33, 2741 & 2749 (1900) 3) Hackh’s (1972), 469-L

Octogen. Ger name for Cyclotetramethylenebognitramine (HMX). See Vol 3, C605-R to C610-R

**OCTOL (Octolite).** Octols are secondary high expl mixts of Octohydro 1,3,5,7-tetranitro-1,3,5,7-tetrazoceine (HMX) (see Vol 3, C605-R to C610-R) and Trinitrotoluene (TNT), usually in the proportions of 3:1. During WWII a need developed for a stable, organic expl possessing a density & de-tonation rate exceeding that of 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX). (See Vol 3, C611-L to C630-L). With F.C. Whitmore’s first large-scale prep in 1942 (Ref 1) of G.F. Wright’s synthesis and naming of HMX (Ref 2), the next higher methylene nitramine homolog of RDX, this need was met. However, to desensitize and render HMX melt-castable requires mixing with a lower melting, more stable expl such as TNT. To maintain the advantages of high density in the cast expl requires that inhomogeneous mixts or slurries be made with TNT because the solubility of HMX or RDX in TNT is only about 5%. The pourability or apparent viscosity of molten TNT slurries of HMX was found to follow rules similar to those governing molten TNT slurries of RDX (also called Cyclotol; see Vol 3, C479)
To achieve the desired cast density for Octol of 1.8g/cc it is necessary that the ratio of HMX:TNT be 3:1. However, at this ratio the apparent viscosity, or efflux, is strongly dependent on the polymorphic variety of HMX used and on its particle size distribution.
In the initial pilot production of Octol (Ref 3) it was found that for the desired efflux of <15 sec, 60-70% of the solid HMX must consist of the beta-polymorph having particle diameters in the range of 500-800 microns. Such precise control of particle size was not possible at that time and early Octol casts were made at approximately 50 secs efflux. The economical production of Octol with a satisfactorily short efflux time continues to present a problem in loading shells with this expl (Refs 4, 11 & 29)
The expl performance of Octol was generally an improvement over that of Cyclotol. Based on the physical and chemical properties of HMX and RDX the following improvements were observed (Ref 4):

<table>
<thead>
<tr>
<th>Type Performance</th>
<th>Expected</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaped Charge Penetration</td>
<td>11%</td>
<td>18.5%</td>
</tr>
<tr>
<td>Rate Acceleration</td>
<td>11%</td>
<td>11%</td>
</tr>
<tr>
<td>Fragment Velocity</td>
<td>11%</td>
<td>7%</td>
</tr>
</tbody>
</table>

The higher specific gravity of 75/25 Octol can make the bursting charge of a shell containing it appreciably heavier than that of the same shell
loaded with Composition B (See Vol 3, C479), the standard at the conclusion of the Korean conflict. For example, the 105mm M1 shell would contain 0.4 pound more expl at a specific gravity of 1.80g/cc or higher. The detonation velocity of cast 75/25 Octol is about 8400m/sec; that of Composition B about 7800m/sec. This difference of 600m/sec in velocity coupled with the heavier bursting charge should yield not only more fragments per shell, but also fragments having a higher initial velocity. For fragmentation-type, ammo this is the kind of improvement most desired. Firing tests showed that the substitution of 75/25 Octol for Composition B in the 105mm M1 shell produced a 15% greater number of fragments having an average 331 foot-seconds greater velocity over identical 180 degree coverage (Ref 6):

Table 1

<table>
<thead>
<tr>
<th>Depth of Penetration (cm)</th>
<th>TNT</th>
<th>Composition B</th>
<th>Octol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>23.8</td>
<td>33.1</td>
<td>37.0</td>
</tr>
<tr>
<td>8</td>
<td>36.2</td>
<td>49.7</td>
<td>57.4</td>
</tr>
<tr>
<td>12</td>
<td>43.2</td>
<td>61.4</td>
<td>68.9</td>
</tr>
<tr>
<td>16</td>
<td>49.1</td>
<td>69.2</td>
<td>78.7</td>
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<td>20</td>
<td>53.0</td>
<td>75.1</td>
<td>85.0</td>
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<td>24</td>
<td>56.2</td>
<td>79.4</td>
<td>89.9</td>
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<tr>
<td>28</td>
<td>58.6</td>
<td>83.0</td>
<td>94.0</td>
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<td>32</td>
<td>61.8</td>
<td>86.2</td>
<td>98.1</td>
</tr>
<tr>
<td>36</td>
<td>64.3</td>
<td>89.3</td>
<td>101.8</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>92.3</td>
<td>105.3</td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td>110.4</td>
</tr>
</tbody>
</table>

Using the eptly determined liner collapse velocities of Composition B, it was found that the foregoing values could be described by a theoretical hydrodynamic code based on detonation rates and expl densities with sufficient accuracy to justify a high degree of confidence in computed penetrations and damage for targets having Brinell hardness numbers between 100 and 300.

The best shaped charge results are obtained with expl comps having the highest detonation pressure HE as illustrated (Ref 20):

The improvement in penetration and damage produced by 105mm shaped charges of Octol over that of Composition B or TNT having the same charge geometry were further documented (Ref 10):
Penetration versus Detonation Pressure

Fig 1 Penetration vs Detonation Pressure of Shaped Charges

Octol, at least at shorter standoffs, gives about 10% deeper penetrations than Composition B, but the latter is better at long standoffs since it seems to lessen perturbance of the shaped-charge jet.

Rather surprisingly, early formulations of Octol were slightly more sensitive to impact than Cyclotol (Ref 4):

<table>
<thead>
<tr>
<th>Composition</th>
<th>Impact Sensitivity (ERL Machine, 2.5kg wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Explosive</td>
<td>RDX 20–24cm, HMX 26–32cm</td>
</tr>
<tr>
<td>Explosive/TNT (70/30)</td>
<td>RDX 53cm, HMX 47cm</td>
</tr>
<tr>
<td>Explosive/TNT (60/40)</td>
<td>RDX 69cm, HMX 52cm</td>
</tr>
</tbody>
</table>

In view of the lower impact sensitivity of HMX, the trend for Octol is most unexpected and was later (Refs 11, 33 & 34) shown to be caused by surface effects. The apparently greater sensitivity of Octol can be mitigated or reversed by control of the particle size distribution and by changes in the surface treatment of the HMX used in Octol compns.

Octol shows a small increase in stability over that of Cyclotol at higher temps which may be sufficient to overcome the marginal stability of Cyclotol in specific cases.

The 7–15% improvement in expl performance of Octol over that of Cyclotol is achieved at a 250–500% increase in cost (depending on purity), which has to be matched against the overall gain.
in performance of specific weapons. For this reason Octol is most actively exploited as a replacement for Cyclotol only in warhead compns of costly weapons where shaped charge penetration or fragmentation is the major criterion of damage production. This includes the smaller guided missiles and some of the more costly air-to-air (Falcon), air-to-surface (Hellfire), and surface-to-air (Chaparral) rockets and missiles (Ref 39), where the warhead cost is only a minor fraction of weapon cost and a 7–15% improvement is well worth the cost increase.

Expls similar to Octol, viz, HMX/TNT/Al/Wax, 47/31/22/3–5, have been prepd and tested for air-blast and underwater effectiveness. The performance improvements that resulted (1–2%) over Cyclotol analogs were not considered worth the additional cost (Ref 4), and other expls are generally exploited for such applications.

In an age of precision use of expls to achieve precise effects, control of and stable spatial arrangement of the expl is required. Certain limitations and problems of this nature arise in the use of composite expls which are cast from inhomogeneous slurries. One problem is the aerodynamic heating which results when ordnance is carried exposed on high-speed aircraft. Missiles in flight experience similar but shorter term heating effects. Aerodynamic heating may be sufficient to produce melting and substantial expansion of the expl charge. The result may be a bud or a round that does not function as intended. Neither will the round function correctly after solidification unless the original spatial arrangement of the bursting charge components is regained. Associated with long-term, high temp cycling of composite expls is the exudation of portions of the expl charge as a result of thermal expansion. Exudation causes the development of cracks within the confined expl charge and an undesirable increase in sensitivity, especially to set-back pressure (Ref 7). A number of additives have been used to improve growth and crack resistance. Initially, the US Navy found that by dispersing ≤1% o-Nitrophenol in the expl melt before casting resulted in a reduction in exudation. Other crack and growth retarders such as Cyclohexanone, 2,4-Dinitroanisole, 2,4-DNT, and both o- and p-Nitrotoluene were all found to have less effect (Ref 12). Subsequently the French replaced TNT with 2,4,6-Trinitro-N-methylaniline or 2,4,6-Trinitro-N,N-dimethylaniline and obtained melt-castable expls that did not melt or exude at temps of up to 125°, but with a predictably lower detonation velocity than that of either Cyclotol or Octol (Ref 18). Analyses of exudates which migrate from technical grade TNT in cast expls revealed that a major constituent was DNT. A highly porous form of calcium silicate (Micro-Cel E) was next tried as an absorbent of the exudate-causing liq of the TNT matrix, but even at the 0.5% level it caused severe cracking of the cast. The purification of TNT to remove DNT and other exudation-causing impurities increased the brittleness of TNT-based cast expls. However, since DNT was known to be an effective plasticizer of NC in propellant formulations, it was found that Octol + 0.45% plasticized high viscosity NC and Octol + 0.3% plasticized cellulose propionate (CP) had the optimum properties for crack resistance, exudation reduction, and least cast charge growth (Ref 19).

The ineffectiveness of Micro-Cel for controlling exudation was conclusively demonstrated during temp-humidity cycling tests conducted on the Chaparral missile. The temp cycle used was from −4° to 103° for a 24-hour period, with missiles held at extremes for a 4-hour period and brought from one extreme to the other in eight hours. Exudate was observed on eleven of twelve missiles submitted to test (Ref 35).

Another variable peculiar to composite, cast expls that must be controlled to achieve precision penetration and predictable destructiveness is the variation in density and compn of the expl within the warhead. In melt-loading operations with Octol, problems occur which do not arise in melt-loading with TNT, Composition B, or Cyclotol. Specifically, there is a large amount of settling of HMX crystals while the charge is still molten. It has been shown that the average percent HMX in a warhead ranges between 70% and 77% whether loaded with 60/40 Octol or 70/30 Octol. Correspondingly, the HMX content of the riser produced is low, often reaching 40%. It was shown that by using 60/40 Octol instead of 70/30 for casting the M18 warhead for the 66mm M72 Light Anti-Tank Weapon (LAW) system, a better cast was obtained with optimum penetration (Ref 13). This improvement was attributed to the better fluidity of the 60/40 expl (Ref 16).

The superior shaped-charge performance of Octol, as indicated previously, is limited by perturbances of the detonation wave front that affects jets. The early emphasis on the precision of the metal parts associated with shaped charges
(Ref 5) was in the 1960's focused on the expl itself. At that time the penetration of confined shaped charges of 4.5 to 5.5 charge diameters was considered acceptable with an ideal value of 7 (Ref 20). Max penetration and damage or hole volume created in armor requires max energy content, which in turn demands high HMX concn, overcoming viscosity problems, reducing air entrapment, with the elimination of microporosity. It is desirable not to use melt-pour temps above 95° to decrease viscosity for a variety of reasons. For example, TNT shrinks from 11 to 12% on solidification, so that if the melt is too viscous during pouring, the entrapped air may not escape prior to solidification. These bubbles are further enlarged by the volume shrinkage of TNT, resulting in a porous cast of low density.

Vacuum casting has been used in Germany by Boelkow B.m.m.H. to achieve more homogeneous casts and eliminate microporosity (Ref 14). Subsequently, Reichel showed that by programming the temp of the entire melting-filling cycle and centrifuging the poured charge at 25000 ft/sec^2 for 10 to 15 minutes, crack-free charges of highest density could be produced. These loading methods were evaluated with 1 kg unconfined shaped charges, 96mm in diameter, incorporating a 60 degree 2mm thick copper liner. Using the product of penetration depth and hole volume at the optimum standoff as a figure of merit (PV), the following comparisons were obtained (Ref 17):

<table>
<thead>
<tr>
<th></th>
<th>Max Penetration (cm)</th>
<th>Hole Volume (cm^3)</th>
<th>PV (cm^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Cast Cyclotol</td>
<td>68</td>
<td>190</td>
<td>13,000</td>
</tr>
<tr>
<td>Vibration Cast Cyclotol</td>
<td>76</td>
<td>240</td>
<td>18,000</td>
</tr>
<tr>
<td>Vibration Cast Octol</td>
<td>82</td>
<td>275</td>
<td>23,000</td>
</tr>
</tbody>
</table>

These expts were designed to defeat the NATO heavy tri-partite target, which requires not only a high basic penetration to overcome the three spaced layers of armor, but requires especially a perfectly aligned jet to defeat the plates at the long compound standoffs. Such precision shaped charges require not only carefully made metal parts but equally precise expl components. The superiority of these more elaborate casting techniques is reflected in the penetration of nearly 9 charge diameters shown in performance chart for Octol (Fig 2).

The feasibility of improving the melt-casting of Octol thru application of ultrasonic energy has been investigated as part of the US Army's general program to upgrade the performance of the LAW. It has been shown that ultrasonic agitation of molten slurries and gel-like materials generally leads to shear-thinning and permits flow even thru small orifices and into complex molds. In the case of Octol, ultrasonic techniques made possible the successful casting of Octol in which the weight percentage of the solid phase HMX is increased above the point at which normal gravity flow ceases. Using ultrasonic activation of either regular or precision LAW warhead bodies in an axially symmetric (longitudinal) mode at 15kHz, it was possible to obtain castings of Octol 80/20, which will not flow under standard melt-casting conditions, that appeared void-free by X-ray. Continued application of ultrasonic energy for 5-10 minutes after filling promoted settling of HMX particles out of the riser funnel into the warhead body, increasing the HMX content to 65% near the base of the cone with a compn gradient declining to about 80% at the fuz end. Similar results were obtained with 75/25 Octol (Ref 22). There is evidence that it is desirable in Octol-filled forward-firing, conical shaped charges, that the heavier HMX settle out of suspension around the base of the liner cone. However, sectioning and analysis shows that even prolonged mechanical agitation, as opposed to ultrasonic activation, does not yield a uniform longitudinal gradient of Octol density or HMX concn along the axis of TOW, DRAGON or SHILLELAGH warheads. These variations in compn are thought to be responsible for erratic penetrations observed with these missiles but cannot at present be verified non-destructively (Refs 30 & 38).

Thus it can be seen that continuous improvements in defensive armor require ever more sophisticated expl technology for its defeat, which in turn results in the escalation of military budgets for conventional warfare. The increased cost of HMX relative to other expls has caused continuing efforts to reduce manuf costs, to improve and more precisely evaluate its effectiveness. In a recent, very painstaking comparison of Cyclotol and Octol, the effects of changes in the compn, density, and diameter of the expl charge upon detonation velocity were determined. HMX was found more ef-
Fig 2  SHAPED CHARGE PERFORMANCE FOR SEVERAL CASTING METHODS
(96mm diameter, 60° Copper Cone, 2mm wall, unconfined)
(Stacked plates, St37 Steel)

Effective than RDX in increasing the density of the charges and charges containing HMX detonated more rapidly; otherwise, the increase in detonation velocity was the same for Cyclotol and Octol. With 40–30% TNT and infinite diameter of charge the results were (Ref 21):

- Increase in Density /% increase A or B, mg/cm³ /%
- Increase in Detonation Velocity/Unit Density, msec/mg/cm³
- Increase in Detonation Velocity /% increase A or B at Constant Density, msec /%
- Detonation Velocity at 65% A or B and Max Density, msec

<table>
<thead>
<tr>
<th></th>
<th>RDX</th>
<th>HMX</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.75</td>
<td>2.85</td>
</tr>
<tr>
<td>B</td>
<td>3.40</td>
<td>3.50</td>
</tr>
<tr>
<td>A</td>
<td>16.0</td>
<td>15.0</td>
</tr>
<tr>
<td>B</td>
<td>8070</td>
<td>8254</td>
</tr>
</tbody>
</table>
A linear relationship between Chapman-Jouguet pressure and density was confirmed for Cyclolol and Octol (Ref 28). Despite the near-equal performance of RDX and HMX at equal densities there appears to be no economical way of making the density of RDX equal to the cast density of HMX. Dinitrobenzene (DNB) has been evaluated as an economical or emergency substitute for TNT but charges prepared with DNB gave somewhat poorer performance than those with TNT. Results indicate that TNB could be used as an emergency replacement for TNT in large-diameter munitions (Ref 25). Active efforts are being made to reduce manuf costs by replacing batch processes with continuous granulation (Ref 23) and continuous melt-pour processes (Ref 26).

Table 4 details the physical, chemical and expl properties of Octol Type I and Type II.

| Table 4                                                                 |
|--------------------------------------------------|---|---|---|
| Properties of Octol Type I and Octol Type II    |
| Composition                                     | Type I | Type II | Refs |
| HMX % C₄H₈O₆N₈                                  | 75     | 70     | 9, 27 |
| TNT % C₇H₅O₆N₃                                 | 25     | 30     | 9, 24, 27 |
| Chemical and Physical Properties                |        |        |     |
| Density (Nominal Cast), g/cc                    | 1.80 to 1.82 | 1.80 to 1.81 | 9, 27 |
| Density (Theoretical Max), g/cc                  | 1.832  | 1.819  | 9, 24, 27 |
| Air Blast                                       |        |        |     |
| Weight of Charge 3022g                          |        |        |     |
| Distance from charge, 10 ft                      |        |        |     |
| Overpressure, psi                                | 37.4   | 37.9   | 27 |
| Impulse, psi - msec                              | 18.1   | 21.2   | 27 |
| Distance from Charge, 15 ft                      |        |        |     |
| Overpressure, psi                                | 13.1   | 14.6   | 27 |
| Impulse, psi - msec                              | 12.5   | 15.5   | 27 |
| Distance from Charge, 20 ft                      |        |        |     |
| Overpressure, psi                                | 7.1    | 6.7    | 27 |
| Impulse, psi - msec                              | 9.1    | 11.2   | 27 |
| Autoignition Temperature, °C                     | 100    | 108    | 27 |
| Explosion Temperature, °C                       | 288    | 289    | 27 |
| Seconds 0.1 (no cap used)                        |        |        |     |
| Seconds 1                                        |        |        |     |
| Seconds 5  (flames erratically)                  | 350    | 335    | 24 |
| Detonation Rate (no confinement — cast)         |        |        |     |
| Density, g/cc                                    | 1.81   | 1.80   | 24 |
| m/sec                                            | 8643   | 8377   | 24 |
| 0.5" x 0.5" x 6", m/sec                          | 8328   | 8241   | 27 |
| 1.0" x 1.0" x 6", m/sec                          | 8396   | 8305   | 27 |
| 1.5" x 2.0" x 6", m/sec                          | 8364   | 8310   | 27 |
| Von Neumann Spike Pressure, kbar                  | 452 ± 10 |        | 15 |
| Chapman-Jouguet Pressure, kbar                    | 314 ± 7  |        | 15 |
| Von Neumann Spike Shock Velocity, m/sec           | 8550 ± 30 |        | 15 |
| Chapman-Jouguet Velocity, m/sec                   | 8550 ± 30 |        | 15 |
| Von Neumann Spike Particle Velocity, m/sec        | 2930 ± 70 |        | 15 |
| Chapman-Jouguet Particle Velocity, m/sec          | 2040 ± 50 |        | 15 |

(Continued)
Table 4 (continuation)
Properties of Octol Type I and Octol Type II

<table>
<thead>
<tr>
<th>Dielectric Properties</th>
<th>Type I</th>
<th>Type II</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance, ohms</td>
<td>$2 \times 10^{10}$</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Resistivity, ohm-cm</td>
<td>$2.99 \times 10^{10}$</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>@ 100c</td>
<td>3.121</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>@ 1 kc</td>
<td>3.070</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>@ 10 kc</td>
<td>3.042</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>@ 100 kc</td>
<td>3.013</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Dielectric Strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.040&quot; thick, v/mil</td>
<td>150</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>.039&quot; thick, v/mil</td>
<td>128.2</td>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

Fragment Velocity, ft/sec

<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th>Type II</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>6159</td>
<td>6139</td>
<td>27</td>
</tr>
<tr>
<td>At 20 ft from sample</td>
<td>5790</td>
<td>5772</td>
<td>27</td>
</tr>
<tr>
<td>M26 Hand Grenade (ave first 6 ft)</td>
<td>5124</td>
<td>–</td>
<td>24</td>
</tr>
</tbody>
</table>

Pit Fragmentation
105mm M1 HE Projectile

<table>
<thead>
<tr>
<th>Number Fragments</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4&quot; – 2 grains</td>
<td>24</td>
</tr>
<tr>
<td>2&quot; – 5 grains</td>
<td>24</td>
</tr>
<tr>
<td>5&quot; – 10 grains</td>
<td>24</td>
</tr>
<tr>
<td>10&quot; – 25 grains</td>
<td>24</td>
</tr>
<tr>
<td>25&quot; – 50 grains</td>
<td>24</td>
</tr>
<tr>
<td>50&quot; – 75 grains</td>
<td>24</td>
</tr>
<tr>
<td>75&quot; – 150 grains</td>
<td>24</td>
</tr>
<tr>
<td>150&quot; – 750 grains</td>
<td>24</td>
</tr>
<tr>
<td>750&quot;–2500 grains</td>
<td>24</td>
</tr>
<tr>
<td>5008</td>
<td>4467</td>
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</table>

Friction Pendulum

<table>
<thead>
<tr>
<th></th>
<th>Unaffected</th>
<th>Unaffected</th>
<th>Refs</th>
</tr>
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<tbody>
<tr>
<td>Steel Shoe</td>
<td></td>
<td></td>
<td>24, 27</td>
</tr>
<tr>
<td>Fiber Shoe</td>
<td></td>
<td></td>
<td>24, 27</td>
</tr>
</tbody>
</table>

Heat of Combustion

<table>
<thead>
<tr>
<th></th>
<th>cal/g</th>
<th>cal/g</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{DE}^T$ H$_2$O(L) (calc)</td>
<td>2676</td>
<td>2722</td>
<td>24</td>
</tr>
<tr>
<td>$\Delta H_{DE}^T$ H$_2$O(G) (calc)</td>
<td>1570</td>
<td>–</td>
<td>32</td>
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</table>

Heat of Explosion

<table>
<thead>
<tr>
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<th>cal/g</th>
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<th>Refs</th>
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<tbody>
<tr>
<td></td>
<td>1131</td>
<td>1074</td>
<td>32</td>
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Heat of Fusion

<table>
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<tr>
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<th>kcal/mole</th>
<th></th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.9% HMX, 23.1% TNT</td>
<td>+2.57</td>
<td>–</td>
<td>32</td>
</tr>
<tr>
<td>cal/g</td>
<td>29.4</td>
<td>–</td>
<td>32</td>
</tr>
</tbody>
</table>

Specific Heat

<table>
<thead>
<tr>
<th></th>
<th>cal/g°C</th>
<th>cal/g°C</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.9% HMX, 23.1% TNT</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>cal/g°C –70°C</td>
<td>0.200</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>cal/g°C –80°C to +80°C</td>
<td>0.240</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>cal/g°C 33°C to 74°C</td>
<td>0.245</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>cal/g°C 90°C to 150°C</td>
<td>0.323</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
### Table 4 (continuation)

**Properties of Octol Type I and Octol Type II**

<table>
<thead>
<tr>
<th>Impact Sensitivity</th>
<th>Type I</th>
<th>Type II</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picatinny Arsenal Apparatus inches</td>
<td>17</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>Sample wt, mg inches</td>
<td>25</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td>Sample wt, mg</td>
<td>15</td>
<td>19</td>
<td>27</td>
</tr>
<tr>
<td>Sample wt, mg</td>
<td>19</td>
<td>20</td>
<td>27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>(-62^\circ)</th>
<th>(-40^\circ)</th>
<th>(23^\circ)</th>
<th>(52^\circ)</th>
<th>(71^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength @ (.05) in/min:</td>
<td>(1182)</td>
<td>(1169)</td>
<td>(1509)</td>
<td>(1022)</td>
<td>(635)</td>
</tr>
<tr>
<td>Stress at rupture, psi</td>
<td>(1182)</td>
<td>(1169)</td>
<td>(1509)</td>
<td>(1022)</td>
<td>(635)</td>
</tr>
<tr>
<td>Compression at rupture, %</td>
<td>(0.21)</td>
<td>(0.23)</td>
<td>(0.20)</td>
<td>(0.26)</td>
<td>(0.23)</td>
</tr>
<tr>
<td>Mod of Elasticity, psi (x 10^3)</td>
<td>(720)</td>
<td>(492)</td>
<td>(1344)</td>
<td>(892)</td>
<td>(526)</td>
</tr>
<tr>
<td>Work to prod rupture, ft-lb/in(^3)</td>
<td>(0.11)</td>
<td>(0.14)</td>
<td>(0.14)</td>
<td>(0.16)</td>
<td>(0.15)</td>
</tr>
<tr>
<td>Impact Strength</td>
<td>(1.80)</td>
<td>(1.88)</td>
<td>(1.81)</td>
<td>(1.76)</td>
<td>(1.81)</td>
</tr>
<tr>
<td>Charpy, inch-pounds</td>
<td>–</td>
<td>–</td>
<td>(1.27)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Izod, inch-pounds</td>
<td>–</td>
<td>–</td>
<td>(1.27)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Shear Strength</td>
<td>(599)</td>
<td>(529)</td>
<td>(769)</td>
<td>(640)</td>
<td>(498)</td>
</tr>
<tr>
<td>Stress at rupture, psi</td>
<td>(599)</td>
<td>(529)</td>
<td>(769)</td>
<td>(640)</td>
<td>(498)</td>
</tr>
<tr>
<td>Torsional Shear @ (36^\circ)/min</td>
<td>(113)</td>
<td>(113)</td>
<td>(113)</td>
<td>(113)</td>
<td>(113)</td>
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<tr>
<td>Stress at rupture, psi</td>
<td>(113)</td>
<td>(113)</td>
<td>(113)</td>
<td>(113)</td>
<td>(113)</td>
</tr>
<tr>
<td>Mod of Elasticity, psi</td>
<td>(101,000)</td>
<td>(101,000)</td>
<td>(101,000)</td>
<td>(101,000)</td>
<td>(101,000)</td>
</tr>
<tr>
<td>Tensile Strength @ (.05) in/min</td>
<td>(88)</td>
<td>(81)</td>
<td>(146)</td>
<td>(113)</td>
<td>(120)</td>
</tr>
<tr>
<td>Stress at rupture, psi</td>
<td>(88)</td>
<td>(81)</td>
<td>(146)</td>
<td>(113)</td>
<td>(120)</td>
</tr>
<tr>
<td>Elongation at rupture, %</td>
<td>(.019)</td>
<td>(.014)</td>
<td>(.010)</td>
<td>(.015)</td>
<td>(.018)</td>
</tr>
<tr>
<td>Mod of Elasticity, psi (x 10^3)</td>
<td>(445)</td>
<td>(678)</td>
<td>(1565)</td>
<td>(1548)</td>
<td>(1102)</td>
</tr>
<tr>
<td>Work to prod rupture, ft-lb/in(^3)</td>
<td>(0.0007)</td>
<td>(.0005)</td>
<td>(.0006)</td>
<td>(.0008)</td>
<td>(.001)</td>
</tr>
</tbody>
</table>

| Sensitivity to Initiation | | | | | |
| Minimum deton charge Lead Azide, g | 0.3 | 0.3 | 24 |

| Sensitivity to Setback Pressure \(\text{psi} @ 71^\circ\) | \(0.1\%\) | \(50\%\) | \(99.9\%\) | \(0.0\%\) |
| Probability of Reaction | \(95000\) | \(119000\) | \(149000\) | \(76000\) | \(80000\) | \(119000\) | \(176000\) | \(92000\) | \(27\) |

| Linear Coefficient of Thermal Expansion \(\% x 10^3 /{^\circ}\text{C}\) | \(-50^\circ\) to \(-20^\circ\) | \(-20^\circ\) to \(+20^\circ\) | \(20^\circ\) to \(+50^\circ\) | \(+50^\circ\) to \(+65^\circ\) |
|---------------------------|--------------|--------------|----------------|----------------|----------------|--------------|--------------|--------------|----------------|
| -50º to -20º | 1.73 | 2.59 | 27 |
| -20º to +20º | 3.38 | 2.75 | 27 |
| 20º to 50º | 7.02 | 7.38 | 27 |
| 50º to 65º | 7.13 | 8.05 | 27 |

<table>
<thead>
<tr>
<th>Vacuum Stability</th>
<th>(\text{ml gas/5g sample/40 hrs})</th>
<th>(120^\circ)</th>
<th>(130^\circ)</th>
<th>(140^\circ)</th>
<th>(150^\circ)</th>
<th>(160^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(120^\circ)</td>
<td>0.39</td>
<td>0.65</td>
<td>24, 27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(130^\circ)</td>
<td>1.13</td>
<td>0.97</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(140^\circ)</td>
<td>2.66</td>
<td>1.50</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(150^\circ)</td>
<td>5.10</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(160^\circ)</td>
<td>–</td>
<td>11</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Uses. In addition to fragmentation and shaped charge applications that have already been mentioned, Octol and Octol-like mixes are employed as oil well formation fracturing agents (Ref 31), and in combination with suitable polyester or polyurethane resin binders to compound high efficiency, special-purpose expls (Refs 36 & 37) with detonation rates of 8400–8690 m/sec, friction sensitivities of 24–36 kg and compression strengths of 710 kg/cm².

Analytical. The quantitative analysis of Octol, Type I and Type II is given in US Military Specification MIL-O-45445A (Ord) (30 Sept 1962) which also lists the following requirements (Ref 8):

- Moisture, % 0.25 max
- Insol particles, number of particles retained on No 60 US standard sieve 5 max
- Acetone insol matter, % 0.10 max
- Viscosity, seconds
  - HMX
    - Type I 15 max
    - Type II 12 max
  - TNT
    - 75.0 ± 2.4 70.0 ± 2.0
    - 25.0 ± 2.0 30.0 ± 2.0

The quantitative analysis procedure involves gravimetric detn of the HMX on a moisture-free basis after benzene extraction of, and differential detn of TNT. Moisture content is detd by conductometric titration of sample in an acetic-sulfuric acid suspension. Acetone insoluble matter is determined gravimetrically.

Written by D. J. VEAL

of Testing Services on High Explosive Devices and the Reduction of Accumulated Data”,


Addtl Refs Not Used in Above Article:


Octyl. Brit designation for Bitetyl or Ditetryl, described as 1,2-Bis(2',4',6'-trinitronitrobenzene)-ethane in Vol 2, B131-R and Vol 5, D1513-L. Urbanisld (Ref) describes it as Hexanitrodiphenyl-ethylenedinitramine

Addl Ref: Urbanisld 3 (1967), 69–70

Odite. An older Brit coal-mine expl contg AN 88 & DNB 12%
Ref: Marshall, Dict (1920), 70

Oerlikon. The two Swiss arms firms of Oerlikon of Zurich and Hispano-Suiza at Geneva dominated the world markets in fast firing 20 and 30mm guns used for anti-aircraft fire, and mounted on armored vehicles for the attack of lightly protected targets. In 1972, Oerlikon obtained a controlling interest in Hispano-Suiza, and the products of the two firms have since been controlled from Zurich. As a result of this takeover, the guns of Hispano origin (see Vol 7, H114-L) now being produced by Oerlikon have been re-designated

Off-Carriage Fire Control. A process of controlling fire on a target with the aid of a sighting device which is not mounted directly on the weapon

Offensive Grenade. A grenade having a light container, designed to kill or injure by blast and concussion, distinguished especially from a fragmentation grenade (see Vol 4, D830 & D831). The offensive grenade is so called because the thrower, being out of range of the grenade’s effects, can continue to advance as he throws and does not
have to take cover. In the US Armed Forces this type of grenade is now obsolete (see Vol 4, 9830-L)
Refs: 1) Ohart (1946), 355 & 359 2) OrdTechTerm (1962), 144-L

Offset Bombing. Any bombing procedure which employs a reference or aiming point other than the actual target. This type of bombing is employed when the target cannot be seen or is a poor reference point. When employed, the compensating factors are either set into the bombsight or computed by the bombardier
Ref: OrdTechTerm (1962), 208-R

Offset Distance (Nuclear). The distance the desired ground zero or actual ground zero is offset from the center of an area target or from a point target

Off-The-Shelf-Items. These items required by the military services which are generally used thru-out the civilian economy and which are available thru normal commercial distribution channels
Ref: OrdTechTerm (1962), 208-R

OFS. Code name for 1-Methyl-5-chlorotetramethylene-1,3,5-trinitramine

OFX. Code name for 1-chloro-2,4,6-trinitro-2,4,6-triazahheptane

Ogive. The curved or tapered front of a projectile. As a geometrical body, a convex solid of revolution in which the generating area is bounded by an arc of a circle, the center of which lies on the side of the axis of revolution opposite to the arc. When applied to a projectile contour the radius of the arc is expressed in calibers, such as “7-caliber ogive”. With a bullet, bomb or other projectile having a fuze forming the nose, the ogive is included between a point where the projectile begins to curve or taper, and a point on the line where fuze and body meet. In other types of projectiles, the nose of the projectile is included as part of the ogive
Ref: OrdTechTerm (1962), 208-R

Ogive, False. A rounded or pointed hollow cap added to the nose of a projectile to improve streamlining. Also called windshield or ballistic cap
Ref: OrdTechTerm (1962), 208-R

Ogive, Rifle Grenade. A hollow metallic item designed for attachment to the forward end of a practice rifle grenade. It cushions the impact and permits reuse of the grenade
Ref: OrdTechTerm (1962), 208-R

Ohlsson, J. V. (1833–1923). Swedish expls specialist, who in collaboration with J.H. Norrbin in 1867, patented the first AN based expl, Ammoniakkrus (See Vol 1, A306-R to A307-L)

Oil-Explosive Combinations. See under Slurry Explosives in Vol 6, E469-R, and under Ammonium Nitrate Blasting Explosives in Vol 1, A341ff

Oils, Nitrated. See under Fats, Fatty Oils, Tallow, Butters, Waxes and Fatty Acids in Vol 6, F8-L to F9-L
Addnl Ref: F. Gehre, “Nitration of Vegetable and Animal Oils”, FrP 398748 (1909) & Colver (1938), 723

Okell’s Powders. Smokeless powds patented in 1899 in Fr and in 1900 in Belg (in collaboration with VanOlegar). The NC in these propIns was prepd by nitration of wood (preferably stripped alder) with 11 parts of mixed acid consisting of 1 p nitric acid (d 1.50g/cc) and 3p of sulfuric acid (d 1.84g/cc). The NC was washed, first with w and then with a soda soln. After drying
at 40–50° to reduce the moisture content to 7–8%, the NC was gelatinized with a mixt contg 78% of eth, 15% of acet and 12% of alc per 100p of NC, and then mixed with other ingredients of smokeless powd. For example; Cannon Powder: NC 80 to 88, plus a mixt of 1p K or AN with 3p Ba nitrate, 20 to 12%; Sporting Powder: NC 94, K nitrate 5 & K dichromate 1%
Ref: Daniel (1902), 589–90

Olates. A compd of an alkalioid or a metal with oleic acid. Al oleate has been used for coating the ingredients of exp mixts to prevent reaction under storage conditions. For example see Buechert's expl in Vol 2, B320-R
Ref: Hackh's (1972), 472-L

Olefins, Nitrated (Nitroolefins)

A series of nitrated and unsaturated hydrocarbons. The base molecule for momenclature purposes is usually called the “ethylene series” because the first member is ethylene, C2H4; hence a molecular type CnH(2n-x)N_xO_2x is derived. Other compds in the series are named after corresponding paraffins by adding to the stem “ene” or “ylene” such as 1-nitro propylene,
C3H5NO2. Olefins with two conjugated double bonds are called “dienes”, such as butadiene. For more than two conjugated double bonds terms such as “triene”, etc., are used (Ref 8)

Olefins can be prepd by numerous methods which are described in textbooks on organic chemistry such as Ref 7

According to Urbanzki (Ref 6), “... Besides adding concentrated HNO3 to olefins, true nitration of olefins thru electrophilic substitution can take place to yield nitroolefins... In 1878 Haitinger (Ref 1) found that nitration of iso-butylene with anhydrous nitric acid led to several products, among which was nitroisobutylene (CH3)C2=CHNO2, in 10% yield

In 1935, Michael and Carlson (Ref 4) reported that with fuming nitric acid, trimethylene gave crystalline 3-nitro-2-methyl-2-butylene in 20% yield:

More recently Petrov and Bulygina (Ref 3) investigated in detail the conditions under which several olefins can be nitrated. They found that good yields could be obtained with concentrated nitric acid reacted with olefins at ca 60°C, and with less concd nitric acid at a slightly higher temp, ie, 80–90°C. Nitration was possible with 20% nitric acid, containing nitric dioxide when reacted at 70°C. Probably, nitric dioxide is the nitrating agent, while the role of nitric acid is to regenerate the NO2 radical...

When olefin hydrocarbons react with nitrogen dioxide or nitrous and nitric anhydride, they are added to a double bond...

By addition of nitrogen dioxide, nitrosates (II) (nitroso-nitrate) or dinitro compds (III) or dinitrites (IV) are obtained. Nitrosates (II) can be oxidized to nitro-nitrates (IIa), viz:

\[
\begin{align*}
N_2O_4 & \rightarrow \text{Nitro-nitrate (Ia)} \\
-CH=CH- & \rightarrow \text{Nitroso-nitrate (II)} \\
\text{NO} & \text{ONO}_2 \\
\text{NO}_2 & \text{ONO}_2
\end{align*}
\]

The addition of N2O4 to compds with conjugated double bonds takes place in a way similar to the addition of halogens to these compds...

Schaarschmidt and Hofmeyer (Ref 2) found that on treating an unsaturated hydrocarbon with N2O4 a mixt of products of the I, II, III and IV types was obtained. Only the dinitro compds of type III were stable. Others underwent decomposition in the following way:

\[
\begin{align*}
-\text{CH} & \rightarrow \text{Nitroso-nitrate (IIa)} \\
-\text{CH} & \rightarrow \text{Nitro-nitrate (Ia)} \\
\text{ONO} & \rightarrow \text{Nitroso-nitrate (IIb)} \\
\text{ONO} & \rightarrow \text{Nitro-nitrate (Ib)} \\
\text{ONO} & \rightarrow \text{Nitro-nitrate (Iv)} \\
\text{ONO} & \rightarrow \text{Nitroso-nitrate (Iv)}
\end{align*}
\]

According to Hass et al (Ref 5), “All nitro olefins polymerize with more or less rapidity. For this reason they should be used promptly after synthesis. The polymerization products are black, viscous materials readily soluble in
acetone and benzene."  

Presented below are selected nitroolefins which may be expl compds

Nitro Allyl Acetate. See under "Nitropolymers", in this Vol

3-Nitroacrylic Acid. See Vol 1, A97-R & L

Dinitrobutanes. See Vol 2, B376-L

Mononitrobutane. See Vol 2, B375-R to B376-L

Trinitrobutane. See Vol 2, B376-L & R

X,X-Dinitrocycropylene or X,X-Dinitrooctylene. See Vol 2, C40-L

2,2-Dibromo-1-Nitro-Ethene (?) (β,β-Dibromo-α-Nitro-Ethylene). CH(NO2)2:CBr2, mw 230.85, N 6.07%, OB to CO2 -17.33%; large, six-sided rhombic prisms; mp 112°. V sol in warm ethanol and insol in w. Prep is by bubbling gaseous bromine into an aq soln of Na styrphate [C6H(NO2)3(OH)(ONa)] Separation from the co-product, bromopropionate, is achieved by washing the ppt with warm ethanol

The compd decomp at 120-25°
Ref: Beil 1, 195

Nitroethylacrylate. See Vol 6, E202-L

Ethylene Nitro. See Vol 6, E282-L & R

1-Chlor-1-Nitro-Ethylene and Polymer. See in this Vol under "Nitropolymers"

Eulite. See Vol 6, E342-R to E343-L

2,5-Dinitrofuran. See Vol 6, F241-L

5-Nitro Furfural-N-Nitriminoquandrina. See Vol 6, F243-L

5-Nitro-3-Ethyl-Hexene.  
CH3.C(NO2).CH.CH(C2.H5)2, mw 157.24, N 8.91%, OB to CO2 -218.77%, greenish yel liq, bp 84° at 1mm, d 0.9551/g/cc at 25°, RI 1.4602 at 25°. Prep is by heating 5-Nitro-3-ethyl-hexanol with a soln of Na carbonate in methanol for eight hrs

The compd decomp very rapidly when distd below atm press
Ref: Beil 1, (845)

3,4-Dinitro-3-Hexene. See Vol 7, H92-R to H93-L

1,1,1,6,6-Hexanitro-3-Hexene. See Vol 7, H93-L

Oleum. Fuming sulfuric acid; a soln of sulfur trioxide in sulfuric acid used as a sulfating and sulphonating agent. See under Acidity in Acids in Vol 1, A88-R to A90-R; Acids Used in Manufacture and Analysis of Explosives in Vol 1, A93-L to A93-R; and under Nitration in this Vol

For analytical procedures, see under Glass Bulbs for Weighing Acids in Vol 6, G78-R to G79-R

Olin Powder. Same as Bull Powder
Oliver, Gen Paul A. (1830—1912). American soldier and inventor in the explos field. He founded the Oliver Powder Co (see below), in which work was done by machinery invented by him. His earliest invention dates back to 1868, and relates to machinery for the manuf of gunpowder. Six addnl patents were granted him between 1868 and 1889. The main feature of these inventions was that gunpowder should be handled in small batches and with an excess of moisture, thereby reducing risk to a minimum, and making violent expls impossible. The ingrediants were first mixed in a vertical rotating tub with rotating stirrers, and then fed to a roller press consisting of smooth and teetbed rollers, in which they were ground together, pressed and combed. From the roller press, the powder went to a continuous belt dryer equipped with a woven wire belt.

Oliver’s method is still used, in a modified form, at some BkPdr plants
Ref: VanGelder & Schlatter (1927), 215–16

Oliver Powder Co. An American company manuf commercial expls, founded shortly after the American Civil War by General P.A. Oliver, near Wilkes Barre, Pa. The original plant was destroyed by fire, and another was constructed at a new location, also near Wilkes Barre. The company was sold to the duPont Co in 1903
Ref: Van Gelder & Schlatter (1927), 215–16

Oliver’s Flameless Dynamite. A safety mining expl, manuf in the last century by the Oliver Powder Company. Another Dynamite manufd by the same company was called Meteor Dynamite
Refs: 1) Daniel (1902), 590 2) VanGelder & Schlatter (1927), 586

Oliver’s Powder. A BkPdr, patented in Eng in 1869, in which peat replaced the charcoal, and K chlorate, desensitized by either wax, lard or rosin replaced the K nitrate. Also see refs under Chlorate Explosives in Vol 2, C205-R
Ref: Daniel (1902), 590

Onager. An ancient weapon consisting of a slinglike catapult which threw stones from a bag or wooden bucket. It was so called after a mythological monster, Onager, which was said to throw stones at its pursuers with its feet

On-Carriage Fire Control. A process of controlling fire on a target with the aid of a sighting device mounted directly on the weapon

Oncin. A twelfth-century weapon having a hooked iron head resembling a one-sided pick

Onit. The name, now obsolete, used by AB Bofors, Nobelkrut, Bofors, Sweden, prior to WWII, to designate Hexogen (Cyclonite or RDX) as the basic material used in Bonits (see Vol 2, B242-R)
Ref: C.M. vonArbin of Bofors Co, private communication with B.T. Fedoroff (March 6, 1963)

Ontos. Designated as the M-50, this US Marine Corps system is a full-track self-propelled direct-fire and antitank weapon. It is armed with six 106mm recoilless rifles, one .30cal machine gun, and four .50cal spotting rifles. It has a top speed of 40mph and a crew of three

Opacifiers in Solid Propellants. Carbon black and other pigments having high energy absorption coeff in the visible spectral range (nigrosine black dye, Prussian blue, methylene blue, etc) have been used as additives (0.1 to 0.5% content) in translucent double-base propmts to provide opacity, and thus prevent malfunction due to ignition below the surface at the site of minor imperfections
According to Crawford (Ref 1) and Hickman (Ref 2), grains of double-base propellant exhibit unstable burning characteristics caused by the formation of minute holes (called worm holes) or cracks in their interior during burning. The intense radiant energy developed on burning can cause the ignition of dust or gases accumulated in these imperfections, and results in simultaneous burning in many areas. The incorporation of opacifiers seems to obviate the formation of these imperfections, and does not allow the radiant energy of burning to penetrate within the propellant grains


Open Ammunition Space. Ground area prepared or improvised for storage of ammo in open areas to supplement magazine space
Ref: OrdTechTerm (1962), 210-L

Open Bomb. In intelligence usage, an undisguised or unconcealed sabotage expl device, distinguished especially from an infernal machine

Opening Charge. A charge of expl necessary to burst ordnance containing gas, incendiary or smoke-producing comps. The expl used for this purpose could not be too vigorous, in order not to scatter the contents excessively. Hand grenades were sometimes "opened" by means of a detonator charged with MF. The Brit during WWI developed an opening charge which was termed Ophorite (see below)
Ref: Marshall 3 (1932), 176–77

Ophorite. A Brit perchlorate expl used during WWI as an opening charge (see above) in incendiary and gas shells and smoke bombs. Its compn was K perchlorate 60, Mg powd 40%. This mix developed extreme heat on ignition, but very little gas, and thus did not scatter the shell or bomb contents excessively, which was desirable
Ref: Marshall 3 (1932), 113–14 & 197

Oppau Disaster. An expln which occurred in Oppau, Ger, on Sept 21, 1921, killing 509 people, injuring 1917, and causing enormous property damage. The catastrophe was caused by the use of HE to break up a hard mass of fertilizer consisting of a mixt of AN and Ammonium sulfate. This method had always been practiced at Oppau because it was believed at that time that AN could not be detoned unless a combustible material was also present, and, in fact, about 20000 charges of HE had been previously used in a similar manner without incident

The Oppau disaster led to an extensive examination of the expl properties of AN and it was decided that it can be expld, although with difficulty, when the material is under strong confinement and is heated or inititated with sufficiently strong force

Notwithstanding these results, the treatment of AN was continued as though it were a combustible material rather than a HE, and numerous explns and fires occurred in succeeding years, the greatest to-date being the "Texas City Disaster" (qv) in 1947. See also Vol 1, A312-L to A313-L, A333-R & A357-L to A363-R

Optical Chronograph. Same as Rotating Drum Chronograph, described briefly under Chronographs in Vol 3, C304-Rff

Optical Methods in Ballistics. See under Cameras, High-Speed Photographic in Vol 2, C13-L to C19-R

Optimum Density. See under Limiting Density in Vol 3, D66-R

Optimum Gun. See under Drozdov, N.F., in Vol 5, D1555-L & R

Optolene. A liq rocket fuel (d 0.9g/cc) consisting of about 50% Visol (vinylisobutylether), 10–20% nitrite, with the remainder being Optol (a coal tar product contg phenol). It was used in the Wasserfall missile in conjunction with conc nitric acid (contg about 10% sulfuric acid), which served as an oxygen carrier. The ratio was 0.24ps of Optolene per 1p of acid. The theoretical sp impulse for this mixt was 214 lb/lb/sec, with only 183 actually being obtained. This value was nearly equal to that obtained using Visol/nitric acid


Orange Powders. Various BlkPdrs manufd in the last century by Laflin and Rand Powder Co at Orange, NJ, USA. Also see under Laflin and Rand Powder Co in Vol 7, L2-R

Ref: Daniel (1902), 400

Orbital Bomb. A satellite contg a nuclear warhead which circles the earth in a low orbit and which can be commanded to descend on a particular target. No such weapons are now known to be operational, and their deployment would be prohibited under the terms of the Outer Space Treaty of 1966. However, this treaty does not prohibit anything making less than a full circle around the earth, hence the FOBS (Fractional Orbital Bombardment System). The FOBS method of nuclear delivery takes advantage of the orbital attack configuration while staying within the terms of the treaty. While a normal ICBM follows a very high parabolic path to target, highly “visible” to defending radars, a weapon in low orbit (≈ 100 miles) can make a sharp descent to earth, thus cutting radar warning time very substantially, to about three minutes. A FOBS path therefore consists of a blast-off movement into low orbit, a partial circle to the target earth zone, and a rapid descent. This would seriously prejudice ABM ballistic missile defense systems as now conceived. There is, however, a loss of accuracy and payload which make FOBS weapons unsuitable for a counterforce role against hardened missile silos


ORDNANCE

Definition. A term that includes, in US usage, nearly all combat weapons of the land, sea and air forces. British military usage generally restricts it to guns of artillery caliber. In its broadest meaning the term includes small arms, ammunition, artillery, mortars, recoilless rifles, field guns, howitzers, bombs, mines, grenades, torpedoes, rockets, rocket launchers, guided missiles, self-propelled mounts, tanks, motor combat vehicles and pyrotechnics. In this sense, it is nearly equivalent to munitions or materiel. Weapons mounted on ships, aircraft or tanks are usually referred to as armament rather than as ordnance

Ordnance Department

History. The US Army organization that formerly, for over 100 years, had responsibility for the design, manufacture and procurement from private industry of weapons, ammunition and vehicles, for the training of personnel in their use, and for their storage, issue and maintenance. The Ordnance Department also served both the Navy and Air Force as directed by a higher authority

The lapel insignia worn by ordnance officers
was a flaming bomb. It is said to be the oldest of US Army insignia, having been adopted in 1832.

In the early years of its history the US Army functioned without a distinct ordnance branch. At first, in 1775, ordnance was the responsibility of a Military Stores Committee; then, from 1776 to 1812, of an officer titled the “Commissary of Artillery Stores” and a secret committee under a “Board of War and Ordnance”.

The formation of the Ordnance Department resulted from four events following cessation of hostilities in 1784. In 1785, the Secretary of War was charged with taking into his care all military stores, equipment, and supplies of the US Army. Second, a “Surveyor of Ordnance” was authorized in 1789. Third, Congress provided for the erection and repair of magazines and arsenals, and for the establishment of national armories. Fourth, in 1795, a “Purveyor of Public Supplies” was appointed to conduct the procurement of all military and naval stores necessary for the service of the USA. Finally, the establishment of the Ordnance Department as a separate corps was effected by Congressional Act of 14 May 1812.

As a post-war economy measure, Ordnance was combined with Artillery in 1821. This proved to be a failure, attested to by high ranking Generals and the War Department, so that the Ordnance Department was again organized as a separate corps by Act of 5 April 1832. An Act of 4 June 1920, amending the National Defense Act, placed the Ordnance Department under the Assistant Secretary of War charged with the business and supervision of procurement of all military stores needed in time of war, and reauthorized permanent commissions in the Department after a period of 20 years of “detailing” officers from other arms or services. In 1942, the Ordnance Department was placed under the Commanding General, Services of Supply (Ref 1)

On 28 June 1950, Public Law 581, known as the Army Reorganization Act, replaced the National Defense Act of 1920, changing the name of the Ordnance Department to Ordnance Corps, and merged Field and Coast Artillery (Ref 2).

On 1 August 1962, a major army reorganiza-
tion was implemented, with the creation of two new Commands, Army Materiel and Combat Development. The Ordnance Corps was eliminated, and its functions and responsibilities were distributed among the following subordinate Commands of the Army Materiel Command (AMC): 1) Missile Command: essentially Army Ordnance Missile Command
2) Munitions Command: essentially a combination of the Ordnance Special Weapons — Ammu-
nition Command and Chemical Corps
3) Weapons and Mobility Command: a combination of the Ordnance Tank — Automotive Com-
mand, the Ordnance Weapons Command, and the Transportation Corps
4) Communications and Electronics Command: the Signal Corps plus Ordnance fire-control radar
5) General Equipment Command: essentially engineer equipment and general supplies and equipment outside the responsibilities of the Defense Supply Agency
6) Test and Evaluation Command: responsible for environmental test centers, proving grounds, and the former Continental Army Command service test centers
7) Supply and Maintenance Command: responsible for the terminal Commands, overseas supply agencies, depots, storage and maintenance facilities

An office of Research and Development was established on the staff of AMC having control over such Laboratories as: Diamond Ordnance Fuze, Ballistics Research, Environmental Research, Materials Research, and Human Engineering (Ref 3).

Based on reports and recommendations of the Army Materiel Acquisition Review Committee (AMARC) on 1 April 1974, a major reorganization of AMC was instituted for completion within four years (Ref 4). The concept of separate development and logistic centers was replaced with Research and Development (R&D) Commands or Materiel Readiness Commands, under the US Army Materiel Development and Readiness Command (DARCOM).

This reorganization represents a clear separation of R&D functions from logistic activities (Ref 5)

Mission. Armories at Springfield, Mass (estb 1777) and Harpers Ferry, West Virginia (estb
1794), together with the ten Arsenals listed below, were established to implement the Ordnance Department:

<table>
<thead>
<tr>
<th>Arsenals</th>
<th>Year Established</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rome, Rome, NY</td>
<td>1813</td>
</tr>
<tr>
<td>Allegheny, Pittsburgh, Pa</td>
<td>1814</td>
</tr>
<tr>
<td>Watervliet, West Troy, NY</td>
<td>1814</td>
</tr>
<tr>
<td>Bellaire, Richmond, Va</td>
<td>1816</td>
</tr>
<tr>
<td>Frankford, Philadelphia, Pa</td>
<td>1816</td>
</tr>
<tr>
<td>Pikesville, Pikesville, Mo</td>
<td>1816</td>
</tr>
<tr>
<td>Washington, Washington, DC</td>
<td>1816</td>
</tr>
<tr>
<td>Watertown, Watertown, Mass</td>
<td>1816</td>
</tr>
<tr>
<td>Augusta, Augusta, Ga</td>
<td>1817</td>
</tr>
<tr>
<td>Baton Rouge, Baton Rouge, La</td>
<td>1819</td>
</tr>
</tbody>
</table>

The mission originally assigned to the Ordnance Department was to design, develop, procure, store, maintain, and supply to the Army such equipment and supplies as are assigned to the Ordnance Department for procurement, in such quantities and at such times as are required to meet the requirements of Army supply programs and other directives of higher authority. It was also charged with training and furnishing specialized ordnance troops to service Commands and units of the field services.

By 1945 there were six manufacturing Arsenals:

<table>
<thead>
<tr>
<th>Arsenals</th>
<th>Year Established</th>
</tr>
</thead>
<tbody>
<tr>
<td>Springfield Armory, Springfield, Mass</td>
<td>1777</td>
</tr>
<tr>
<td>Watervliet, West Troy, NY</td>
<td>1814</td>
</tr>
<tr>
<td>Frankford, Philadelphia, Pa</td>
<td>1816</td>
</tr>
<tr>
<td>Watertown, Watertown, Mass</td>
<td>1816</td>
</tr>
<tr>
<td>Rock Island, Rock Island, Ill</td>
<td>1863</td>
</tr>
<tr>
<td>Picatinny, Dover, NJ</td>
<td>1880</td>
</tr>
</tbody>
</table>

Each Arsenal had a standard mission: Under the general direction of the Chief of the Industrial Service, and with reference to the assigned material, each Arsenal designs and develops new and improved items, and in an emergency manufactures and supplies certain standard items; maintains and develops the knowledge of production, provides for the application of new manufacturing techniques; maintains pilot production lines in step with the industrial arts and operates them continuously for immediate use in supplying early demands of war; and acts thereafter as control and advisory center for the major production assumed by industry at large; provides engineering supervision and inspection standards relative to all production of assigned materiel; carries on the necessary activities related to the above.

Organization. The monolithic structure of the Ordnance Department culminated in 1945 with the following organization and responsibilities:

1) Office of Chief of Ordnance
   a) Special Advisory Staff: Leaders of Industry, Finance, and other spheres to assist in formulating policies and procedures for efficient accomplishment of ordnance mission.
   b) General Office: Performs executive and administrative duties which are common to all activities.
   c) Military Plans and Training Service: Training of Ordnance military personnel and planning for the betterment of ordnance service in the Army.
   d) Research and Development Service: Plans and executes progressive plans for research and experimental development of new and improved ordnance material, and new, improved substitute materials for ordnance use.
   e) Industrial Service: Procures, inspects, and accepts all ordnance material and spare parts, performing all related engineering work.
   f) Field Service: Stores, issues, inspects, repairs, modifies, and maintains ordnance material and ammunition in assigned ordnance installations.

2) Field Installations
   a) Specialized Centers and Suboffices: To provide centralized control over decentralized operations and industries such as Cannon Suboffice at Watervliet, Small Arms Ammunition at Frankford, and Inspection Gage and Fire Control Suboffices at Rock Island.
   b) Manufacturing Arsenals (6): To act primarily as centers for technical expertise and development, rather than as manufacturing plants.
   c) Procurement Districts (13): To carry designs and specifications thru procurement to manufacture in civilian industry. Performs final inspection of completed item.
   d) Proving Grounds: Conduct field work of
designing, developing, testing and inspection of ordnance assigned them
e) Government Owned Manufacturing Plants (69): Produce ammunition (56), artillery (2) and small arms materiel (11)
f) Depots: Store ordnance items for issue (Ref 1)
The current organizational concept is directed at establishing individual development centers to emphasize the acquisition process. For ordnance items these centers will consist of:
a) Ammunition Development Center: responsible for small and large caliber weapon systems, chemical systems, and ballistics research
b) Harry Diamond Development Center: responsible for all non-communication related electronic research and development disciplines, such as fuzes, sensors, lasers, electrophysics, and improved electronics technology and electrical components
c) Missile Development Center: responsible for development and initial acquisition of Army missile systems
See also under "Army Ordnance Corps (US)" in Vol 1, A485-R, and "Arsenal" in Vol 1, A489-R

Written by D. J. VEAL

4) J.R. Deane, Jr, Army, 68-72 (Oct 1975)
5) Anon, Army Research & Development Magazine, 4 (Jan-Feb 1976)

Organ Gun. A piece of ordnance with numerous gun barrels arranged side by side and capable of being fired simultaneously. In the fourteenth to the seventeenth century as many as 160 barrels were sometimes so arranged. Also see under Orgues

Organic Promoters. To an expl mixt contg TNT, PA, Nitronaphthalene, and an oxidizer such as AN or Ba nitrate, is added one or more aliphatic or aromatic compds in which the molecular length, calc'd from values of atomic radii and bond angles given in the Ref, is within 0.1A° of being equal to 3.89, 4.19, 4.84 or 5.13A°. Suitable organic promoters are ethyl acetate, methyl propionate, propanol, butanol; propionic, lactic and butyric acids; butyric aldehyde, benzyl alcohol, salicylic acid, 1,2-dichloroethylene, or glycine
Ref: US Powder Co, BritP 497145 (1938); CanadP 380077 (1939) & CA 33, 4040 (1939)

Organic Vapors Explosion Hazard, Reduction of. See under Explosion Hazards of Organic Vapors, Reduction of, in Vol 6, E373-L; Detonation (and Explosion), Hazards (Dangers) of, in Vol 4, D366-L to D367-R; and D245-L

Orgues (Organs). Firearms consisting of a number of barrels firing simultaneously, invented in Fr in the sixteenth century by Pedro Navarro, an engineer in Louis XII's court. He designed some 200 orgues, his later masterpieces being 2 feet long and firing some 50 shots at once. It should be noted that previous to Navarro, in the fifteenth century, Leonardo daVinci invented multi-barrel guns which can be considered as distant ancestors of the recent anti-aircraft "pompons"
Ref: J.E. Newman, "The Tools of War", Double-day Doran, NY (1943), 51

Oriastites. Explo similar to Meganites (see in this Vol), but contg no nitrated corozo (ivory nut). One of the varieties was: NG 60, nitrated wood (nitrolignite) 20, and Na nitrate 20%
Ref: Daniel (1902), 434 & 591

Oriental (Powder). Mixt of BlkPdr, K chloride and ligneous materials such as tanbark, sawdust, etc. Also see Vol 2, C205-R
Ref: Daniel (1902), 591
Origin—Identification of TNT. A study was conducted at PicArsn to demonstrate the feasibility of associating trace organic impurities in TNT to its origin of manufacture. TNT samples from the process lines at three US Army Ammunition Plants were analyzed for their mono-, di-, and trinitrotoluene isomer purity contents by gas chromatography. The isomer impurity profiles of TNT samples, representing a series of lots manifest over a two-month period were found to remain constant for a given plant. In addition, significant differences were shown to exist in the kind, number and concn of isomers among the representative samples from the three plants. Based on these results, the trace organic impurity profile of TNT is shown to be related to its origin.


Ormites. Mining expls contg nitrates as the chief ingredients, authorized for use in Engf in 1898.

Ref: Daniel (1902), 591

Orsman’s Explosives. Several expls were patented in Engf by W.J. Orsman between 1896 and 1900. One was called Amvis (see Vol 1, A393-R); others were: a) A mining expl obtained when one p of finely pulped cellulose or the slightly nitrated product was blended with one p of hot chloronitrobenzene and 20p of powdered AN (BritP of 1896–7); b) A mining expl prepd by mixing one p of lampblack with one p of DNB and 24p of powdered AN (BritP of 1899–90)

Ref: Daniel (1902), 592

Ortho-Nitroaromatic Compounds; Hazards in Handling. The refs discuss the expl properties of o-nitrobenzoyl chloride and o-nitrophenacetyl chloride, both of which are likely to expld when heated to over 100°. It is suggested that these compds be prepd and utilized in soln without isolation of the acid chloride

Refs: 1) N.C. Cook & F.C. Whitmore, C&EN 23, 2394 (1945) & CA 40, 1034 (1946)

Orthophosphates. Expls characterized by the evolution of N on heating may be effectively stabilized by the addition of approx 1% of a neutral mixt of alkali metal dihydrogen orthophosphate (ie, NaH2PO4) and dialkali metal hydrogen orthophosphate (ie, Na2HPO4)

Ref: E. Whitworth & J.C. Hornel, USP 2470733 (1949) & CA 43, 5594 (1949)

Oscillograph. A cathode-ray oscilloscope in which a photographic or other permanent record is produced by the electron beam of a cathode-ray tube. A cathode-ray oscilloscope is a test instrument that uses a cathode-ray tube to make visible on a fluorescent screen the instantaneous values and waveforms of electrical quantities that are rapidly varying as a function of time.

In the ordnance field, oscillographs are used in chronographs and chronometers to determine the muzzle velocity of ammos and proplns, as well as the velocity of detonation of expls, See under Chronographs in Vol 3, C304-R to C319-L


03 (O-Three) Explosive. See under Explosives 03 or Promethees in Vol 6, E363-L

Otter (or Paravana). A protective underwater device which, when towed with a wire rope from a fitting on the bow of a ship, rides out from the ship’s side and cuts the cables of anchored mines. The mines then rise to the surface, where they can be seen and destroyed.

OTTO. A liq monopropellant used in a hot gas generator to give increased speed, range and depth to the US Navy's Mk48 torpedo. 

Ottoon's Military Dynamite. See under PATR 1760 in Vol 5, D1611-R

Out-of-Line Safety. A term descriptive of a method by which detonator safety or bore safety is attained. In the safe condition, one or more components of the fuze or booster exploy train are in a non-aligned condition with respect to the other components, so that normal functioning cannot occur.
Ref: OrdTechTerm (1962), 216-R

Output Characteristics. The characteristics of an expl component which determine the form and magnitude of the energy released. See under Output Tests in Vol 4, D1084ff.

Outrigger. Used mainly in antiaircraft artillery. An outrigger might be called a form of trail in that it aids in stabilizing the weapon. The outriggers are hinged, allowing them to be folded either horizontally or vertically for traveling, and extended in a horizontal plane when the mount is emplaced. Four outriggers are usually attached to each mobile gun mount.
Ref: OrdTechTerm (1962), 216-R

Outrigger Torpedoes. Expl charges attached to a long pole and carried in small boats toward enemy vessels. When the vessels are reached, the torpedoes are placed against their hulls and fired, either by percussing or by electrical caps. This primitive and suicidal method of "torpedoing" ships was attempted by the Russians during the war of 1877-78, and several Turkish ships were sunk, together with the attacking forces.

Overhit (Oversaturate). To hit a target with more destructive force than necessary to accomplish the desired amount of damage.
Ref: OrdTechTerm (1962), 216-R

Overpressure. The pressure resulting from the blast wave of an expl. It is referred to as positive when it exceeds atm pressure and negative during the passage of the wave when resulting pressures are less than atm pressure. Peak overpressure is the highest overpressure resulting from the blast wave.

Overspin (Oversatbilization). In a spin stabilized projectile, when the rate of spin is too great for the particular design of projectile, it becomes oversatbilable and its nose does not turn downward as it passes the summit of the trajectory and follows the descending branch. In such cases the projectile is said to have "overspin" or "oversatbilization.
Ref: OrdTechTerm (1962), 217-L

Oxalate Blasting Powders. Mining safety expls invented in Engl by Groves and Hann in 1897-98 and manufd by the Oxalate Blasting Powder Co at Gatebeck (Westmoreland), which later became the Nitrates Explosives Co, Ltd. These expls were a modification of BlkPdr in which sulfur was partially or entirely replaced by one or more of the following: oxalic acid, oxalates of Amn, K or Na (simple or double), borax, boric acid, etc, each of which could contain of hydration. The purpose of these substitutions was to obtain expls with a cool flame, so that they could be safely used in gaseous mines.
Refs: 1) Daniel (1902), 592—3; 2) Cond-ChemDict (1942 Ed only), 290
Oxalate Carbonite and Oxalate Gelignite. Explosives containing oxalates as “cooling agents”, manufactured in England by the Nobel Explosives Co. Ltd beginning in 1899. See under Cooling Agents or Coolers in Vol 3, C511
Ref: Daniel (1902), 593

LIST OF OXALATE COMPOUNDS

Barium Oxalate. BaC₂O₄, mw 225.36, colorless crystals; mp, decomp. 400°C to CO+BaCO₃; loses CO above 346°C; d 2.568g/cc, v sl sol in w (0.0093g/cc at 18°C, 0.0228g/cc at 100°C), sol in acids & Ammonium chloride, insol in alc. Prep from Ca formate in Ref 1, Q₇ in kcal/mole at 18°C, BaC₂O₄ (e), −327.6; at 25°C, BaC₂O₄.4H₂O (c), −363.7; at 18°C, BaC₂O₄·H₂O (ppt), −397.37; at 25°C, BaC₂O₄·2H₂O, −470.1; at 25°C, BaC₂O₄·3H₂O, −575.73 (Refs 5, 6 & 7)

Ba oxalate is poisonous, an eye, nose, throat and skin irritant, and produces dermatitis. It is a fire and explosion hazard, dangerous when heated to decompn, and emits toxic fumes (Refs 5 & 9)

It has been used as a retardant in pyrots, imparting some green color to burning compns (Refs 5 & 8), and as an ingredient of gunflash simulators (Ref 2 & 3)

The requirements of the US Armed Forces are contained in Mil Spec JAN-B-660, “Barium Oxalate (For Use In Ammunition)”, (5 Aug 1948): Color – white; moisture – 0.3% max; material insol in 10% HCl soln – 0.5% max; material sol in water – 0.3% max; water sol alkalinity – 0.1% max; water sol acidity – the water extract shall not be acid to methyl orange; barium oxalate – 92% min; calcium salts – 0.5% max; grit – none; granulation, thru No 100 US Standard Sieve – 90% min; apparent density – 0.50g/ml max

Refs: 1) Gmelin, Syst Nr 30; 8th Ed (1932), 144–149; supplement (1960), 303–305
2) O.G. Dunkle, “Study Toward Reducing the Smoke Effects From Flash Eliminating Agents”, PATR 705 (1936)
3) D. Hart, “Development of Compositions and Materials for Simulator, Gunflash, No 3, Mk 1”, PATR 1520 (1945)
4) L. Marder, MAF 28, 467 (1954)

Calcium Oxalate (Monohydrate). CaC₂O₄·H₂O, mw 164.12, colorless monoclinic crystals; mp, loses H₂O at 200°C, d 2.2g/cc; insol in w, acet ac & alc, sol in acids. Prep from Ca formate in Ref 1, and Ca cyanamide in Ref 2. Q₇ at 298°CK, −399.1kcal/mole; free energy of formation at 298°CK, −350.6kcal/mole; entropy at 298°CK, 37.28kcal/mole; heat capacity, 36.40 cal/degree/mole (solid) (Refs 5, 6, 7 & 8)

Ca oxalate is corrosive and produces local irritation. It has a caustic effect on mouth, esophagus and stomach, and can cause severe damage to kidneys (Refs 6 & 9). It can be dangerous when heated to decomposes because of toxic fumes (Ref 6)

Ca oxalate has been used as a retardant in pyrots, imparting a pink color to burning compns (Ref 3), and as an ingredient of gunflash simulators (Ref 4)

The requirements of the US Armed Forces are detailed in Mil Spec JAN-C-628, “Calcium Oxalate (For Use in Ammunition)”, (30 June 1948): Color – white; moisture – 0.5% max; material insol in 10% HCl soln – 0.5% max; material sol in water – 0.4%; barium salts – 0.5% max; calcium – 26.6% min; oxalate – 58.4% min; grit – none; granulation – thru No 100 US Standard sieve – 99% min; apparent density – 0.60g/ml max

Refs: 1) H. Breit, USP 1622991 (1927)
2) I. Barsky & J. Buchanan, JACS 53, 1270 (1931)
3) G.J. Schlaft “Modification of M-8 Flare Composition to Increase Candlepower”, PATR 676 (1935)
4) D. Hart, “Development of Compositions and Materials for Simulator, Gunflash, No 3, Mk 1”, PATR 1520 (1945)
5) E.S. Freeman & B. Carroll, JPhysChem 63, 394 (1958)
(Oct 1963), 45–6  7) Merck (1968), 194-L  

Lead Oxalate. PbC₂O₄, mw 295.23; wh, heavy powd; mp, decomp 300°; d 5.28g/cc. Insol in w, sl sol in acetic, sol in dil nitric ac & fixed alkali hydroxides. *Poisonous!*

Warren (Ref 1) evaluated Pb oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

- **Drop Test.** (BurMines app; 2kg wt) 100+ inches
- **Expln Temp Test, 5 sec.** > 500°
- **Sand Test (200g bomb)**
  - Initiation by fuse, g sand crushed 0
  - Initiation by 0.3g MF, g sand crushed 0

There is no US Mil Spec for Pb oxalate

**Refs:** 1) K.S. Warren, "Properties of Possible Constituents of Primer Compositions. Metallic Salts of Chlorous and Oxalic Acids", PATR 1389 (1944) 2) Merck (1968), 613-R

Mercurox Oxalate. Hg₂C₂O₄, mw 489.22, wh cryst powd. Prepd by Souchay & Lenfsen (Ref 2) by treating sol mercurox salts, such as the nitrate, with oxalic acid. Insol in cold w, alc & eth; decompd by hot w; insol in dil sulfuric acid; sol in dil hydrochloric and nitric acids

Explds on impact (Ref 2); does not expid or deflagrate on heating or rubbing in a porcelain mortar (Ref 3)

There is no US Mil Spec for Mercurox oxalate

**Refs:** 1) Beil 2, 516 & [489] 2) A. Souchay & E. Lenfsen, Ann 103, 308 (1857) 3) A. Langhans, SS 15, 89–90 (1920)

Mercuric Oxalate. HgC₂O₄, mw 288.61, wh cryst powd; mp, decompd. Prepd by Souchay & Lenfsen (Ref 2) by adding an ag soln of mercuric nitrate to an ag soln of oxalic acid.

Insol in cold w, difficulty sol in hot w and dil sulfuric acid; sol in dil hydrochloric and nitric acids

Explds on heating or impact (Ref 2); deflagrates on rubbing in a porcelain mortar (Ref 3)


Warren (Ref 4) evaluated mercuric oxalate as a possible replacement for MF in primer compns, and concluded that it lacked the sensitivity necessary for an initiating agent. Sensitivity data obtained are given below:

- **Drop Test.** (BurMines app; 2kg wt) 95 inches
- **Expln Temp Test, 5 sec.** 170°
- **Sand Test (200g bomb)**
  - Initiation by fuse, g sand crushed 0
  - Initiation by 0.3g MF, g sand crushed 6.5

There is no US Mil Spec for Mercuric oxalate


**Note:** R. Philip reported that Hg oxalates are always present as impurities in commercial MF, and that the determination of Hg is not sufficient to give the true fulminate content [R. Philip, SS 7, 110, 156, 180, 198 & 221 (1912)]

Potassium Oxalate. K₂C₂O₄·H₂O, mw 184.23; colorl, odorless crysts; mp, loses H₂O at about 160°, when ignited is converted into carbonate without appreciable charring; d 2.13g/cc, sol in 3p of w. Can be prepd by heating a mixt of K formate or carbonate with oxalic acid and a small amt of K hydroxide, with subsequent extraction of w. Highly toxic by inhalation and ingestion

K oxalate was used as a cooling agent in mining expls such as Oxalate Blasting Powder (see in this Vol) and Gelatine-Properlit (see in Vol 6, G52)

There is no US Mil Spec for K oxalate


Silver Oxalate. Ag₂C₂O₄, mw 303.78, wh cryst powd; mp, decompd violently between 130° & 190° (see below); d 5.03g/cc. Sol in 240000p of w, moderately concd nitric acid, and ammonia. Can be prepd by mixing cold solns of oxalic acid and Ag nitrate (Refs 1, 2 & 6)
Berthelot (Ref 4) states that Ag oxalate expels very energetically when subjected to a shock or when heated to 130°. Wöhler found that the salt expd at 140° when heated in a current of hydrogen (Ref 2). Hoitsema (Ref 5), however, gives an expn temp of 190°.

Taylor & Buxton (Ref 6) report that Ag oxalate is insensitive to impact. It expd with a weak puff when dropped on a hot metal surface at 260°, and at 232° on slow heating. It was not ignited by the spit of a fuse when compressed in a detonator capsule, and was not detonated by 0.25g of MF.

Warren (Ref 7) evaluated Ag oxalate as a possible replacement for MF in primer comps, and concluded that it lacked the sensitivity necessary for an igniting agent. Sensitivity data obtained are given below:

Drop Test (BurMines app; 2kg wt) 90 inches
Expln Temp Test, 5 sec 210°
Sand Test (200g bomb)
Initiation by fuse, g sand crushed 0
Initiation by 0.3g MF, g sand crushed 0

There is no US Mil Spec for Ag oxalate.


Sodium Oxalate. Na₂C₂O₄, mw 134.01; white, odorless, crys powd; mp 250–270° with decompn; d 2.34g/cc. Sol in w (3.7g/100g at 20°, 6.33g/100g at 100°), insol in alc. Can be prep’d by neutralizing an q soln of oxalic acid with Na carbonate (Refs 1, 10, 11 & 13)

Na oxalate is a strong poison! It is corrosive and produces local irritation. Taken orally, it has a caustic effect on the mouth, esophagus and stomach, and can cause severe damage to the kidneys (Refs 10 & 11). It is dangerous when heated to decompn, emitting toxic fumes (Ref 10).

Na oxalate has been used as a cooling agent in mining expls, such as Oxalate Blasting Powders (see in this Vol) and Tremonite (qv), as well as in some Fr permissible expls contg NG (Ref 3, p 420). It has been evaluated as a flash reducing agent in propnts (Ref 4), and is used in pyrots to impart a yellow color and reduce burning rate (Refs 5, 6, 7, 8, 9, 10, 12 & 14).

The requirements of the US Armed Forces are described in Mil Spec JAN-S-210, “Sodium Oxalate (Technical Grade)”, (15 May 1945).

This specification covers one grade of sodium oxalate, furnished in the following classes as specified in the contract or order: class a, class b, class c, and shall conform to the following requirements: Moisture — 0.50% max; oxalate purity — 99.0% min; insoluble matter — 0.50% max; sodium acid oxalate — 1.50% max; granulation — shall conform to the following requirements using US Standard sieves.

<table>
<thead>
<tr>
<th>Thru US Std Sieve (μm)</th>
<th>Class a</th>
<th>Class b</th>
<th>Class c</th>
</tr>
</thead>
<tbody>
<tr>
<td>420 micron (No 40)</td>
<td>99</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>250 micron (No 60)</td>
<td>—</td>
<td>99.9</td>
<td>—</td>
</tr>
<tr>
<td>149 micron (No 100)</td>
<td>90</td>
<td>—</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Strontium Oxalate, Anhydrous and Monohydrate. SrC₂O₄ and SrC₂H₄·H₂O; mw 183.65 & 193.67; colorless. For monohydrate, required for soln of 1 p: 2000p of w. 1900p of 3.5% acet ac, 1115p of 23% acet ac; less sol in 35% acet ac; readily sol in dil hydrochloric or nitric acids. Heat of formation, kcal/mol at 18°, anhyd; at const press, ~327.7; at const vol, ~326.5. Free energy of formation, kcal/mol at 18°, monohydrate: (ε) ~360.8. The monohydrate begins to lose H₂O at 43°, with all gone by 177°. On further heating the wt remains const up to 400°. It dissociates into Sr carbonate and dangerous CO over the range 400–520° (Refs 3 & 5).

Sr oxalate can be prepd by treating hot aq oxalate or oxalic acid soln with a hot aq soln of a Sr salt (Ref 1).

Sr oxalate is highly toxic, corrosive and produces local irritation. When taken orally it may have a caustic effect on the mouth, esophagus and stomach (Ref 5).

Both SrC₂O₄ and SrC₂O₄·H₂O are used as burning rate retardants and to impart a scarlet color to burning pyrotic comps (Refs 2, 4, 6 & 7).

The requirements of the US Armed Forces are detailed in Mil Spec MIL-S-12210A, "Strontium Oxalate", (11 Sept 1952): Strontium oxalate shall be of the following grades as specified: Grade A — anhydrous strontium oxalate Grade B — hydrated strontium oxalate, and shall conform to the physical and chemical properties listed in Table 1

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Grade A</th>
<th>Grade B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>Moisture, percent, max</td>
<td>0.25</td>
<td>10.0</td>
</tr>
<tr>
<td>Strontium oxalate, percent, min</td>
<td>94.0</td>
<td>84.0</td>
</tr>
<tr>
<td>Iron, percent, max</td>
<td>0.01</td>
<td>—</td>
</tr>
<tr>
<td>Ammonium compounds, percent</td>
<td>None</td>
<td>—</td>
</tr>
<tr>
<td>Granulation</td>
<td>Thru No 60 sieve, percent, min</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Thru No 140 sieve, percent, min</td>
<td>99.0</td>
</tr>
</tbody>
</table>

Strontium oxalate shall be free of barium compounds, and shall contain not more than a slight amount of calcium compounds. Conformance with these requirements shall be determined by means of a flame test


Oxalidhydroxamic Acid (Oxalsäurehydroxamid, Oxalidhydroxamsäure, Dihydroxyoxamid, or Aethandihydroxamsäure in Ger). C₂H₂O₄N₂, mw 120.02, N 23.33%, OB to CO₂ –26.66%. Three isomers have been reported:

a) Oxalidhydroxamsäure of H. Lossen: HO.NH.CO.COH.NOH, prisms, mp 165° followed by expln. It was prepd by H. Lossen in 1869 (Ref 2) by the action of hydroxyxamine on the ethyl ester of oxalic acid. Other methods of prepn are given in Ref 1. Sl sol in cold w, insol in acctic ac. Forms salts (Amm, Ba, Ca, Fe, K, Ag & hydroxylamine), most of which expld between 130° and 180°

b) Oxalidhydroxamsäure of W. Lossen & P. Behrend: HO.NH.CO.C(OH).NOH, unknown in the free state, but several of its salts were prepd and proved to be expln (Ref 3).

BaC₂H₂O₄N₂; mp, explds violently; was prepd by the interaction of ethyl oxalate, Ba hydroxide soln and hydroxylaminohydrochloride. Ca, Cu and Ag salts were also prepd; they all expld at about 50°

c) Oxalidhydroxamsäure of N. Paolini: HO.N:C(OH).C(OH).NOH, white hygr prisms from eth & alc, mp 82–83°, decomp 90°, explds when heated rapidly. It was prepd by the action of benzene sulfoxhydroxamic acid on glyoxal. V sol in w, sl sol in eth & alc, sol in ether plus alc (Ref 4). It forms salts, some of which are expln. Hofmann & Ehrhardt (Ref 5) prepd its Cu-K salt (K₂Cu₂C₂H₄O₈N₄) and stated that it expld at 180°. However, this salt, as well as other oxalidhydroxamic acids prepd by Hofmann & Ehrhardt, were
later claimed to be impure (Ref 6)

Refs: 1) Beil 1, 555, (240) & (512)
2) H. Lossen, Ann 160, 314−22 (1869)
3) W. Lossen & P. Behrend, Ber 27, 1105 (1894)
4) N. Paolini, GazzChimItal 37, II, 89 (1907) & JCS 92, Abs 1, 832 (1907)
5) K.A. Hofmann & V. Ehrhardt, Ber 46, 1463 (1913)
6) G. Ponzio & R. Sismondi, GazzChimItal 56, 709 (1926)

Oxalic Acid, (COOH)₂.2H₂O, mw 126.07; monoclinic tablets, prisms, granules; mp 101−102°, giving off H₂O of crystn and starting to sublime; d 1.653g/cc at 18.5/4°. One g dissolves in about 7ml w, 2ml boiling w, 2.5ml alc, 1.8ml boiling alc, 100ml eth, 5.5ml glycerol; insol in benz, chlf, petr eth (Refs 2 & 3)

Oxalic acid was formerly manufd by fusion of cellulose matter, eg sawdust, with Na hydroxide or by oxidation with nitric acid. It is now made by passing CO into coned Na hydroxide or by heating Na formate in the presence of Na hydroxide or Na carbonate (Refs 1 & 2)

Oxalic acid is caustic and corrosive to the skin and mucous membranes. Ingestion may cause severe gastroenteritis with vomiting, diarrhea and melena. Renal damage can occur as result of formation of excessive Ca oxalate. Severe poisoning can end fatally. Tolerance, 1 mg per m³ of air (Refs 2, 3 & 4)

The US Armed Forces requirements for oxalic acid are covered by Federal Spec 0-0-690a, “Oxalic Acid, Dihydrate, Technical”, (July 1, 1968). It details three classes: class 1—large crystals, class 2—small crystals, and class 3—powder. It requires a min assay of 99.0% by wt as H₂C₂O₄.2H₂O, a max ash content of 0.20% by wt, and the following particle size characteristics using US Standard sieves:

For uses of oxalic acid, see under oxalic acid, anhydrous, below

Refs: 1) Beil 2, 505, (219), [475] & (1534)

Oxalic Acid, Anhydrous (Ethanedioic Acid, Aethanedioûre or Klessiûre in Ger). HO₂.C.CO₂.H, mw 90.04, orthorhombic crysts from glac acet ac; mp, 189.5° dec, subl best at 157°; d 1.9g/cc. Sol in w (10p at 20°, 120p at 100°); sol in alc (24p at 15°); sl sol in eth (1.3p at 15°) (Refs 1 & 6)

Used as a cooling agent in some mining expls (Ref 2), such as Oxalate Blasting Powder (see in this Vol), and as a flash reducing agent in propblnts. V. Vender proposed heating oxalic acid with glycerin in order to obtain an expl compd, Dinitroformin (see Vol 6, F173-R), suitable as an antifreeze in Dynamites (Ref 3).

Oxalic acid can also be used for the prepn of glycerol monooformin, CH₂O.H.CHOH.CH₂OH+ (COOH)₂ →CH₂(0.CHO).CHOH.CH₂OH+CO₂+H₂O, which on nitratin gives an expl dinitrate (Ref 4 & Vol 6, F173-R). The Socié Anonyme d’Explosifs et de Produits Chimiques in 1907 proposed the use of oxalic acid for the prepn of oxanulide, from which the expl Hexenitrooxanitride is obtained (Ref 5)

Refs: 1) Beil 2, 502−39, (217−22), [471−83] & (1534)
2) Daniel (1902), 592 3) Naôûm, NG (1928), 197 & 374 4) Davis (1943), 222 5) Colver (1938), 387 & 711 6) Merck (1968), 772-L

Oxalic Acid Dihydrizide (Oxalylhydrozide, Oxalhydrizide, Oxalsûre-dihydrizid in Ger). H₂N.NH.CO.CO.NH.NH₂, mw 118.02, N 47.46%, OB to CO₂ −67.78%, needles from w;

---

Table 1
Particle Size Characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1</td>
</tr>
<tr>
<td>Passing thru a 2.00mm (No 10) sieve</td>
<td>-</td>
</tr>
<tr>
<td>Retained on a 1.41mm (No 14) sieve</td>
<td>85(min)</td>
</tr>
<tr>
<td>Retained on a 500-micron (No 35) sieve</td>
<td>-</td>
</tr>
<tr>
<td>Passing thru a 74-micron (No 200) sieve</td>
<td>-</td>
</tr>
</tbody>
</table>
mp, starts to decompose at 235° (Ref 2), melts with decomposition 244–45° (Ref 6), explodes at 548° (Ref 5); sol in w, nearly insol in abs alc, eth, chlor and benz.

It was first prepared by Curtius et al (Ref 2) by treating 1 mol of oxalic acid ethyl ester with 2 mols of hydrazine hydrate in alc. Other preparations are described by Bülow (Ref 3) and Borsche (Ref 6).

Oxalylhydrazide is an expI (Ref 5), and forms salts, some of which are expI, i.e.: Cu-K salt, K₂Cu(C₂H₄O₂N₄)₂, pale yel needles, sol in w and dil alcalies, explodes at 270° (Ref 4).


Oxalic Acid, Salts of. Bertholet (Ref 2) in 1883 noticed that some salts of oxalic acid, e.g. mercuric or silver, have the properties of primary expI. According to Urbanski (Ref 14), although they have no practical application as initiators, it is interesting from a theoretical point of view, due chiefly to the fact that the general equation for the decomposition of oxalates is: A_{solid} -> B_{solid} + C_{gas}. Thus it is similar to the decomposition of azides.

There have been several papers on Ag oxalate—Ag₂C₂O₄. Macdonald and Hinselwood (Ref 7) confirmed the Bertholet equation, according to which the only products of decomposition of Ag oxalate are metallic Ag and CO₂. Benton and Cunningham (Ref 9) found that the rate of thermal decomposition of Ag oxalate may be increased by previously exposing it to ultraviolet radiation. During the thermal decomposition of Ag oxalate, fragments of metallic Ag are formed. This has been confirmed by conductivity measurements (Ref 10) or by X-ray examination (Ref 11). Tompkins (Ref 12) investigated the thermal decomposition of Ag oxalate at 110–130°. Its decomposes, in his opinion, is similar to that of Ba azide.

Mercuric oxalate (HgC₂O₄) appears to undergo decompose by a somewhat different mechanism with the formation of Hg and mercurous oxalate as intermediate products before full decomposes occurs (Ref 13).

Other more exotic Hg derivatives of oxalic acid include the following:

**Ethane Hexamercarbide** (Di-anhydro-hexakis-[hydroxymercuri]-sitan or Aethanmercarbide in Ger.). HO.Hg(OH₂)₂.C(C(H₂)₂O)H₂.OH, mw 1293.56, lemon yel powd; mp, 220° decomposes violently at 230°; sol in w, shows basic character. It can be prepared by refluxing yellow mercuric oxide in alc with K hydroxide for 36 hrs (Ref 3); other methods are described in Refs 6 & 8. Ref 5 states that rubbing the dry material between sheets of paper is sufficient to cause an exph. Its perchlorates expI on heating or friction with the evolution of green light (Ref 4, p 1336), as does its picrate (Ref 3, p 1907).

**Tris-[Hydroxymercuril]-Acetic Acid.** (HO.Hg)₃.C.COOH, mw 709.79, pale yel powd, puffs off on heating. Can be prepared by passing CO₂ thru tris-[Chloromercuri]-acetic acid [Cl(Hg)₃.C.COOH] dissolved in cold dil KOH.

Its derivative, Anhydro-tris-[hydroxymercuril]-acetic acid, HO.Hg(OH₂)₂.C.COOH, mw 671.79, was prepared by Hofmann (Ref 4, pp 1330–32) in two forms, alkali-sol and alkali-insol. The nitrate of the first form puffs off on heating, while the nitrate of the second form sparks on heating, but does not exph.


**Oxalyl-ethyl ester Azide** (Azido-oxalic acid Ethyl-ester, Azido-oxalsäure-äthylester or Oxalsäure-
Oxamic Acid Azide (Azido Oxamate, Oxamidoazide, Oxamidäureazid or Oxalsäure-amid-azid in Ger). H₃N.COCO₂.N₃, mw 114.02, N 49.11%, OB to CO₂ —42.09%, crystals from acet + petr eth; mp, expls violently ca 115° or on rubbing. Can be prepd by treating the hydradize of oxamic acid with Na nitrate in w
Ref's: 1) Beil 2, (244) 2) T. Curtius & K. Hochshwender, JPraktChem 91, 434 (1915) & JCS 108 (I), 787 (1915)

Oxamide (Oxalamide, Oxalic acid diamide, Ethanediamide, Ethanedioic acid diamide).
H₃N.COCO₂.NH₂, mw 88.07, N 31.81%, OB to CO₂ —72.67%; white, odorl powd, triclinic needles; mp 417—19° decomp, d 1.667g/cc, sparingly sol in hot w, alc, insol in eth (Ref's 1, 5 & 6). Q² 202.64 kcal/mole, Q¹ 121.39 kcal/mole (Ref 3). Can be prepd from formamide by glow-discharge electrolysis (Ref 4)

Oxamide has been used as a stabilizer for NC preps (Ref 6), as a coolant in proplnt formulations because the amt of smoke contributed by it was small (Ref 2), and as a component of Oxamide Explosive Composition (see below)

The requirements of the US Armed Forces are detailed in Mil Spec MIL-O-60883, "Oxamide" (15 December 1967) as follows:
mob content — 0.1% max; purity — 99.0% min; acidity (as oxalic acid) — 0.05% max; pH — 6.5 ± 1.5; residue on ignition — 0.05% max; particle size, grade A — 4 ± 0.2 microns; granulation, grade B — thru US Standard Sieve No 30, 100% min; thru US Standard Sieve No 325, 80% min

US Mil Spec MIL-O-60371, "Oxamide Explosive Composition" (29 June 1966), contains requirements for the following compns:

Composition B
<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>6.7 ± 0.5%</td>
</tr>
<tr>
<td>Oxamide</td>
<td>10.0 ± 0.5%</td>
</tr>
</tbody>
</table>

Composition R
<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>50.0 ± 2.0%</td>
</tr>
<tr>
<td>TNT</td>
<td>40.0 ± 1.0%</td>
</tr>
<tr>
<td>Oxamide</td>
<td>10.0 ± 0.5%</td>
</tr>
<tr>
<td>Wax, Desensitizing</td>
<td>1.0 ± 0.5%</td>
</tr>
</tbody>
</table>

In addition to analytical requirements for the above constituents, the Spec contains a moisture requirement of 0.25% max, an insol particles requirement, and a viscosity requirement

Oxanilide and Derivatives

Oxanilide (N,N'-Diphenyloxamide, Oxaläuredianilid in Ger). C₈H₅.NH.COCO₂.NH.C₆H₅, mw 240.25, N 11.65%, OB to CO₂ —213.11%, white plates from benz, mp 247–54°, bp > 320°, insol in cold & hot w & eth, sl sol in hot alc, fairly sol in benz. It can be prepd by heating aniline with oxalic acid (Ref 2)

Oxanilide has been used as an antiflash agent in proplnts, and as a coolant and burning rate reducer in fuzes powders (Ref 3). According to Davis (Ref 4), it functions well as an antiflash agent if it is distributed thruout a proplnt charge, but not if it is loaded into a gun in separate bags, like the Ger Vorlage or the Fr Sachets Antilueurs

On nitration, oxanilide yields expľ tetra- and hexanitrites (see below)
Ref's: 1) Bell 12, 284, (207) & [165] 2) A.D. Macallum, JSCI 42, 469T (1923) 3) S. Livingston, “Develop Non-Slagging Fuz Powder for the T-14 Fuze”, PATR 843 (1937) 4) Davis (1943), 326
2,4,2',4'-Tetranitro-oxanilide (TNO).

\[ \text{C}_4\text{H}_8\text{N}_4\text{O}_10, \text{mw 420, N 20.0\%, OB to CO}_2 \text{84\%, OB to CO } -31\%, \text{yellow needles from NB, mp 313° decomn (Ref 6)} \]

**Preparation.**

**Oxanilide:** Two parts of oxalic acid are mixed with one part of aniline in a round bottom flask. The mixt is stirred and heated until the reaction is complete as evidenced by the cessation of effervescence. The mass is cooled to room temp, poured into several volumes of water (21–24°), filtered on a Büchner funnel and washed free of oxalic acid with water and then washed free of aniline with acet. The oxanilide is air dried to remove the acet and then dried at 100–110°.

**Tetranitro-oxanilide (TNO):** A 5% round bottom flask is equipped with a stirrer of a type which will produce a downward “swirl”. The flask is surrounded with a water jacket for hot and cold water. Fifteen hundred grams (1.5 kilograms) of 98% plant grade nitric acid is placed into the flask. Five hundred (500) grams of oxanilide is slowly added to the acid under rapid agitation while the temp is maintained below 40°. After the addition of the oxanilide is completed (2½–3 hrs), the agitation is continued 10–15 minutes. The temp is then raised to 80° over a period of one hour and maintained at 80–85° for 3 hours. The acid slurry is then cooled to room temp and drowed by pouring over cracked ice. The product is filtered on a Büchner and washed with water until it is almost acid free. The filter cake is placed in a beaker and sufficient water added to form a “slurry”. Live steam is run into the “slurry” under agitation for 10 minutes. The slurry is filtered and the residue washed. The latter treatment of the “slurry” is repeated until the wash water is found to be neutral to litmus paper. The TNO is washed with alc, then acet, air dried and finally dried at 100–110°. Yield 90 to 97.5% of theoretical (Ref 6)

**Origin.** A.G. Perkins in 1892 obtained TNO directly by heating a soln of finely powdered oxanilide in nitric acid. He also obtained the same compd by the action of a cooled mixt of nitric and sulfuric acids on oxanilide and pptg the product by pouring the soln into w (Ref 2)

**Impact Sensitivity.** PicArsn app, 11mg sample; 30 inches

**Friction Pendulum Test.** Steel shoe: unaffected; Fiber shoe: unaffected

**Explosion Temperature.** 5 second (no cap used): 392°

**100° Heat Test.** Loss 1st 48 hrs: 0.07%; loss 2nd 48 hrs: 0.00%; explosion in 100 hrs: none

**Hygroscopicity.** % wt gain at 30°, 90% RH: trace

**Vacuum Stability Test.** cc/40 hrs at 90°: none; 100°: none; 120°: 0.11

**Sand Romb Test (200g).** 16.3g sand

**Sensitivity to Initiation.** Minimum detonating charge, g: LA: 0.20; Tetryl: 0.25

**Solubility.** g/100cc solvent in: water at 100°: <0.10; NB at 150°, <15. Sol in acet ac, nitric acid, caustic potash; v sol in dimethyl formamide; insol in ethyl alc, benz, butyl acetate, CCl4 & ethyl ether (Ref 6)

**Uses.** Component of BikPdr type formulations, delay and pyrot compns (Refs 3, 4 & 5)


2,4,6,2',4',6'-Hexanitro-oxanilide (HNO).
**Preparation.** To prepare Hexanitro-oxanilide, first prepare Tetranitro-oxanilide as described above under the entry "2,4,2',4'-Tetranitro-oxanilide (TNO)"

A 1.5K round bottom flask is equipped with a stirrer of the type which causes a downward swirl. The flask is jacketed for hot and cold w. 187g of nitric acid of specific gravity 1.49g/cc (commercial grade) is placed into the flask and 100g of sulfuric acid is added to the nitric acid under agitation. The mixed acid is cooled to 10°. 29.2g of Tetranitro-oxanilide is slowly added to the mixed acid under rapid agitation maintaining the temp at 8–10°. After the addition of the TNO is completed (approximately 25 minutes) the temp is raised to 85° over a period of 2 hours and held at 85–90° for one hour. The Hexanitro-oxanilide (HNO) "slurry" is filtered on a Büchner funnel and purified as explained under "Tetranitro-oxanilide" (Ref 10) Origin.

A.G. Perkin in 1892 obtained Hexanitro-oxanilide directly by heating to boiling a soln of Tetranitro-oxanilide (TNO) in a mixt of sulfuric and nitric acids. He also prep'd the same compd from oxanilide by the action of a boiling mixt of fuming nitric and sulfuric acids (Ref 2)

**Impact Sensitivity.** PicArsn app, 12mg sample: 15 inches

**Fricton Pendulum Test.** Steel shoe: unaffected;
Fiber shoe: unaffected

**Explosion Temperature.** 5 second (no cap used): 384°

**100° Heat Test.** Loss 1st 48 hrs: 0.07%; loss 2nd 48 hrs: 0.05%; explosion in 100 hrs: none

**Hygroscopicity.** % wt gain at 25°, 90% RH: 0.19

**Vacuum Stability Test.** cc/40 hrs at 100°: 0.40

**Sand Bomb Test (200g).** 52.1g sand

**Sensitivity to Initiation.** Minimum detonating charge, g: LA: 0.30; Tetryl: 0.25

**Exudation on Dry Storage.** None

**Solubility.** g/100cc solvent in: water at 100°: 0.10; NB at 20°: <3; at 210°, 5. V soln in dimethylformamide, sol in nitric acid, insol in ethyl alc, acet, benz, butyl acet, CCl₄, ethyl ether & acet ac (Ref 10)

**Uses.** Ingredient of igniter and pyrot comps (Refs 6, 7, 8 & 9). Recommended in the older literature as an expl having approx the same power as TNT, and in mixts with AN, chlorates or perchlorates (Refs 3, 4 & 5)

**Refs:**
1. Beil, 12, 767
2. A.G. Perkin, JCS 61, 462 (1892)
3. Société Anonyme d'Explo- sitis (Paris), FrP 391106 (1907) & CA 4, 2733 (1910)
4. Colver (1938), 387 & 711
5. Davis (1943), 188
6. S. Livingston, "Preparation of Tetranitro Carbazole", PicArsn Chemical Research Laboratory Rept 136330 (11 April 1951)
7. L. Gowen & R. Dwiggens, "Case Gun Ignition Studies", NAVORD 2321 (1952)
9. S. Livingston, "Development of Improved Ignition Type Powders", PATR 2267 (1956)

**Oxaziranes.** A class of organic compds containing the ring structure

\[ \text{O} \quad \text{O} \]

S.T. Putnam & R.H. Earle, Jr, of the Hercules Powder Co reported that an attempt to prepare bis-(2-tert-butyl)oxazirane) caused an expln resulting in severe hand injuries to a researcher (Ref 2). The compd, after being prep'd according to the method of W.D. Emmons (Ref 1).

was transferred to a 2 oz wide-mouth bottle with a metal spatula. This was then covered with a polyethylene film and a screw cap, and stored overnight at 35°F. On the following day the material was being transferred to a round-bottom flask, again using a metal spatula, when the expln took place.

The cause of the expln was not detd, but Putnam and Earle feel that it was probably caused by the presence of a small amt of some highly unstable contaminant. In making the compd they obtained a 29.4% yield, compared w. th 51% reported by Emmons.

**Refs:**
2. Anon, C&EN 36, 46 (9 June 1958)
OXAZOLIDONE AND DERIVATIVES

Oxazolidone-(2) (Anhydro-[β-oxyethyl]-carbamic acid). H₂C.NH.CO.O.CH₂, mw 87.08, N 16.09%, crs from alc, mp 88–91°, bp ca 200° at 21mm. Sol in w and alc, sl sol in benz. Can be prepd by passing phosgene into a clif soln of β-aminoethanol in the presence of Na bicarbonate.

On nitration it forms expl nitro and nitroso derivatives (see below)

Refs: 1) Beil 27, 135 & (259) 2) A.P. Franchimont & A. Lublin, Rec 21, 47 (1902) & JCS 82, Abs 1, 427 (1902)

3-Nitrooxazolidone-(2). H₂C(NO₂).CO.O.CH₂, mw 132.08, N 21.21%, OB to CO₂ −48.5%, needles from benz, mp 111°. Insol in w, sol in benz. It was prepd by Franchimont & Lublin (Ref 2) by boiling a mix of oxazolidone & concd nitric acid.

Nitrooxazolidone was prepd and examined in Canada during WWII and was found to be very expl. Its impact sensitivity is 0.48 TNT (less sensitive), and it could not be detonated with a No 8 blasting cap (Ref 3)

Refs: 1) Beil 27, 136 2) A.P. Franchimont & A. Lublin, Rec 21, 49 (1902) & JCS 82, Abs 1, 427 (1902) 3) Blatt, OSRD 2014 (1944)

3-Nitros oxazolidone-(2). H₂C(NO).CO.O.CH₂, mw 116.08, N 24.14%, OB to CO₂ −68.82%, needles from ethyl acet petr eth, mp 53°. Can be prepd by treating oxazolidone with K nitrite in dil HCl at 0°, or by bubbling NO₂ thru an ethereal soln of oxazolidone (Ref 2). Sol in w, v sol in alc, ethyl acet & benz, sl sol in petr eth.

Nitros oxazolidone decomps on heating, often explosively, and ignites on contact with concd K hydroxide

Refs: 1) Beil 27, 136 2) S. Gabriel, Ber 38, 2410 (1905)

OXIDES, INORGANIC

Binary compds, formed from oxygen by combination of as many as eight oxygen atoms with another element, with the exception of carbon and hydrogen, are called inorganic oxides. These compds are crysol below their fp and can usually be reduced to the nonoxygen element with either hydrogen or carbon by heating above RT. The inorganic oxides according to Partington (Ref 15) are classified into different groups, among which are:

a) Acidic oxides, such as P₂O₅ and SiO₂, which react with bases to form salts containing the non-metallic element of the acidic oxide in the anion

b) Basic oxides, such as Na₂O, CaO, FeO and PbO, which react with acids to form salts in which the element of the oxide is in the cation.

It is to be noted that Na₂O unites violently with w to form NaOH as does CaO to form Ca(OH)₂, while Fe and PbO react very slowly. If a metal forms more than one oxide, the lower oxide may be more basic, for example FeO and Fe₂O₃, where Fe(OH)₂ is the stronger base.

c) Amphoteric oxides, such as ZnO and Al₂O₃, act as weakly basic oxides in the presence of strong acids, and weakly acidic oxides in the presence of strong bases.

d) Higher oxides include dioxides which are further classified into (1) peroxides or superoxides when they contain the −O−O− group, such as Na₂O₂ and BaO₂, which give H₂O₂ when reacted with acids, (see under Peroxides in this Vol) and (2) dioxides or polyoxides when the oxygen atoms are linked separately by double bonds, such as O=Mn=O and O=Pb=O.

e) Mixed oxides which are compds of two oxides so that the element has different valences, such as Pb₃O₄=2PbO, PbO₂ and Fe₃O₄=FeO, Fe₂O₃.

Inorganic oxides are usually prepd by intimate contact between the element and oxygen or air. The reaction may be rapid and exothermic, as when finely divided pyrophoric materials ignite spontaneously in air or oxygen. Examples of these materials are iron, lead and phosphorus. Or, the reaction may be slow as when iron oxidizes when exposed to ordinary moist air, or when aluminum oxidizes at the surface upon exposure to air. Much of the time oxidation requires an elevated temp of well over 1000° and may be accompanied by the evolution of large quantities of heat and light, as in the oxidation of aluminum powder used in ordinance applica-
tions such as expls (see Vol 1, A146-L to A152-R), rocket proplnts (see Vol 1, A152-R), and pyrots (see Vol 1, A152-R to A154-L (including Magnesium)).

Other methods of prepn include the heating of nitrates, as for Na₂O₃; of carbonates, as for CaO; or of hydroxides, as for MgO. Of course, many inorganic oxides occur in nature as ores. Examples of these are Fe₂O₃, Fe₃O₄ and SnO₂. For individual methods of prepn, see under the selected inorganic oxides described below.

Several toxic effects of inorganic oxides become evident when oxides are inhaled in a finely powdered form. A high concn of powdered oxides can lead to asphyxiation on short exposure or lung cancer at somewhat lower concns if the exposure occurs over a prolonged period. Blood poisoning can occur if an inorganic oxide such as As₂O₃ is allowed to penetrate an open wound. Of course, oxides such as Na₂O and CaO have a markedly corrosive action on all body tissue (Ref 38). The specific toxicities of selected inorganic oxides are presented below.

Inorganic oxides have many ordnance applications in batteries, ceramics, expls, nuclear energy and propn syts, proplnts, and pyrots. A brief dissertation on each of these applications is now presented.

Much work has been accomplished using oxides to provide electrochemical energy sources in the form of batteries. The use of manganese dioxide in dry cell electrolyte to prevent polarization by hydrogen is well known. More recent uses of oxides in storeable electrical energy sources is shown in the study undertaken by Streigle (Ref 37) concerning a silver oxide—zinc battery for USA Ord. The Spec required a wt of 12 lbs, a voltage of 24V, a current of 0.15Ampere, (5Ampere pulse), and a 50 hr operating life. It was decided that a KOH electrolyte (31% in soln) temp control could be readily obtb by isotopic heating using a radioisotope heater. Again, oxides were used in a study to find the best radioisotope for the purpose. Those considered were: glass (SiO₂), CeO₂, Cr₂O₃, Tm₂O₃, PuO₂. The radiation hazard and the costs involved eliminated all candidates but a 20% concn of Pu-238 or plutonium oxide.

The ordnance applications of inorganic oxides as ceramics are of considerable interest. One such application is that of armor which has the advantages of having a lower density than steel, being easier to form than steel, and in one application, being optically transparent. Indeed, the development of a process for the production of useful sizes of optically transparent ceramic armor made from MgO was the objective of a program conducted by Niesse and Vasilos (Ref 42). Evolved was a process for making 8 x 8 inch magnesia sheets using vacuum hot pressing, annealing the hot pressed discs, polishing and coating the magnesia surfaces and bonding the magnesia sheets together. The yield of optically transparent magnesia discs averaged 35%. The majority of rejects were caused by gases in the initial pressing powder leaving clustred microvoids which resulted in hazy areas. In another program to fabricate ceramic armor by Rhodes and Delai (Ref 47), dense boron suboxide was processed by hot pressing. The correct adjustment of mfg parameters produced perfect billets 4 inches in diam by 0.375 inches thick. Other work on ceramic armor has been conducted using fused silica (Ref 22). This work resulted in a silica plate possessing 50% greater HEAT stopping power than a fused silica reference standard. A study made by Ryszewski (Ref 34) on beryllium oxide ceramics shows four applications of ord interest, ie, nuclear reactors, electronics, turbines and rocket nozzles. Nuclear reactor applications will be described below. The electronic application concerns the use of BeO as a heat sink. In this very important function the thermal resistance of a BeO insulator (or rise in temp/watt of elect power applied) is negligible. Hence, the power input with sintered beryllia transistor insulation can be increased 100% and more above mica or anodized aluminum insulators previously used. For the rocket nozzle application, models of nozzles prepd by the National Beryllia Corp, each having an inner W surface of W-BeO gradient body consisting of concentric layers of W-BeO compn contg an increasing percentage of BeO with increasing radius of the nozzle cross-section, were tested by firing with a proplnt at 3200º, which developed more than 110 atm press without any evidence of erosion or of thermal shock damage.

Fused silica impregnated with either silicon or epoxy resin can also be used for this application. These silica compn nozzles are able to
withstand the conditions of over 400 psi and over 2100° flame temp which are imposed in the oxyhydrogen test rocket motor during its firing.

Again, according to Ref 34, BeO offers a possible solution to the problem of developing turbine components which will withstand the thermal stresses arising from supersonic speeds of mach 2 to mach 3 encountered in aircraft flight. The feasibility of this approach is based on the superior shock resistivity of beryllia (BeO), and the possibility of producing gradient BeO/metal turbine blades and other components which will retain their integrity under the imposed flight conditions. The above Ref, as well as the work of Ormsby and Brown (Ref 44), describes the use of lithia-alumina-silicate (Li2O, 1 to 4) Al2O3 (2 to 8) SiO2 or fused beryllia for use as radomes in aircraft or missile applications. Several expit sintered beryllia radomes have been prep'd by the National Beryllia Corp, using the slip-cast method. This technique fabricated radomes with a d of 2.88 g/cc and dielectric coefficients of 6.57 at 8.5 x 10^9 hertz and 5.87 at 3.3 x 10^10 hertz. The General Dynamics Corp (Ref 33) has also done considerable work on slipcasting radomes of fused silica for SAM missiles. In another use of inorganic oxides by Greskovitch and Woods (Ref 43), yttrium oxides have been used as a laser host material having both high peak and high avg power characteristics. A unique ceramic application is the work of Talty (Ref 55) who has studied yttria (yttrium oxides stabilized zirconia (zirconium oxides) as a material used in regenerative storage heaters for high temp blow-down wind tunnels. Tinsley (Ref 48) has also used heaters comprised of the oxides of zirconium, aluminum, and yttrium to operate a full-scale, intermittent airflow, high enthalpy, high press test facility for aircraft and missile models in the mach 2 to 8 flight regime at 1850 psi and 445°F

In explosives, calcium oxide has been used for many years according to Daniel (Ref 1) in devices such as the Igniter of JaroLinet. This is a device used in blasting operations, and consists of a double cartridge containing compressed CaO in one end and a flammable mixt (usually a mixt of 50% KClO3 and 50% mercuric fulminate) in the other end. The flammable end is attached to a MF blasting cap which was inserted in the main Dynamite charge (or other blasting expl). In order to produce an expln, a small quantity of w is brought into contact with the compressed CaO and heat is evolved which ignites the KClO3-Hg(OCN)2 mixt. The MF cap is detonated, thus exploding the main charge (Ref 1, p 16). Another expl use for CaO was proposed in 1853 for breaking coal seams. It was called Sir George Elliott's "Quicklime Explosive." The technique consisted of compressing freshly prep'd quicklime into dry bore-holes. When w is added, an expansion is produced as the result of the reaction CaO + H2O = Ca(OH)2, as well as from the pressure developed by the superheated steam produced from the w by the heat of reaction. The expansion ruptures the bore-hole and breaks apart the surrounding layers of coal (Ref 1, p 133). There are also the Cartridges of Smith and Moore which contained a perforated iron tube (connected with a source of w) placed inside a paper cartridge of compressed Ca(OH)2 (Ref 1, p 133). Another device, the Cartridges of Arnout (Belgium), depended upon the heat produced by the action of w on CaO to produce instantaneous evapn of liq sulfur dioxide or nitrous oxide (Ref 1, p 134). Still another device, the Cartridge of Steinau (1887), used a perforated paper cartridge filled with CaO, in the center of which was a glass bottle containing w and a second smaller bottle of sulfuric acid. The cartridge was inserted in a bore-hole of the same diameter, and w was introduced. The heat developed by the CaO broke the w bottle and then the sulfuric acid bottle. The pressure produced by the superheated steam evolved then broke open the surrounding coal seams (Ref 1, p 738). Blais and Picard (Ref 22) have defined Specs and processes for the mfg of CaO to be used to manuf white calcium cyanamide which is the intermediary compd used to prep Guanidine Nitrate (see Vol 6, G150-R to 151-R). Oxides such as ClO2, XeO3 and XeO4 can be considered expls and are described as such below. Varrato (Ref 7) found that Ammonium Nitrate (AN) containing 0.5% zinc oxide was satisfactory for use in Amatoi, as it did not cake or change in granulation after 7 months storage. According to Clear (Ref 12) there are several deleterious effects occasioned by the presence of iron or
copper oxides on TNT under conditions of increased pressure. It was found that these oxides cause decreases in ignition temp and an increase in the rate of decompn of TNT, with mixts of TNT and iron oxide igniting at temps as low as 90°. Both SiO₂ and red ferric oxide are used to increase the sensitivity of gelatinous detonators in an invention of Schlüter and Meyer (Ref 24). The improvement in sensitivity is due to the addn of 4.0 to 25% of SiO₂ with a grain size of <0.2mm and a d of 2.4g/cc to the formulation collodion cotton 0.8−2.0, TNT 0−6.0, AN 40−60, wood powder 0−5.0, and red Fe oxide 0.2%. A safer procedure for the use of Al, Mg, or Zn powders in expls and pyrots is provided by an invention of Ekd and Eldth (Ref 26) in which these powders are inactivated by oxidation with subsequent impregnation using a high mol wt fatty acid. Another use of oxides in expls is that of silicon dioxide in the form of powdered glass and later powdered quartz, has been used in the Gravel Mine series of expl devices to provide adequate initiating sensitivity (Refs 29, 31, 32, 40 & 41). These miniature mines were designed to be initiated with as little as 30 lbs of force after being sown by aircraft, artillery or vehicles. The usual compn was quartz 50.0, silica 1.5, RDX 29.8, and LA 18.7%

In the field of nuclear energy and propulsion systems inorganic oxides have been used as fuel elements and as radiation moderators, reflectors and shields. Belle and Jones (Ref 19) have compiled data on uranium oxide in which topics such as the properties, preparation, activation, effect of other metal oxide addns, sintering, power cycling of fuel rods, etc, of UO₂ are discussed. Fast breeder fuel cycling based on a core fuel mixt of UO₂ and PuO₂ is discussed in Ref 20. The use of various oxides in nuclear energy are also described in Refs 23, 25 and 27. The role of beryllium oxide in nuclear reactor and propulsion systems is comprehensively discussed by Rothman in Ref 30 and by Ryshkewitch in Ref 34.

In propellants (see Propellants, Solid in this Vol), some of the work reported by Dunkle (Ref 6) examined the addn of flash reducing agents versus smoke evolved in proplnt comunds for the cal .50 rifle. The oxides examined included aluminum oxide, stannic oxide, silicon dioxide, ferric oxide and, after proplnt ignition, nickel and tellurium oxides from the metal additives in the proplnts. It was found that the greater the relative abs humidity, the greater the quantity or optical density of smoke produced by a proplnt, and that elimination of flash is dependent upon the mp of the inorganic residue, ie, residues with mp's of about 1400° such as aluminim and stannic oxides, are flashless and (specifically for these compds) smokeless, while low mp inorganic residues are good flash-suppressors. Clear (Ref 14) has reported that aluminum oxide has no adverse action on the storage stability of 2.36" rocket proplnt, but in intimate mixts of the proplnt with the oxide some reaction occurs at 120°, however, proplnts using alumina are feasible. Oxides have been used in proplnts for gas generating purposes, such as Hutchinson's invention (Ref 16), which uses self-sustained, exothermic, nondetonating, gas-evolving decompn reactions to actuate pressure-operated mechanical devices, for blasting operations, proplns of rockets, etc. These reactions are obtb by igniting local areas of Nitroglycerine and/or Guanidine Nitrate comnps contg 0.25−1.0 asbestos fiber and 0.2−10.0 wt% of H₂MoO₄, CeO₂ or U₂O₅. According to Johnson et al (Ref 51) such gas generating systems can employ pyrot-type metal oxides together with solid proplnts to generate electrophilic gases. Such gases consist of H₂MoO₄, HReO₄ and HBO₂. The oxides included in the proplnts are molybdenum oxides, boron oxides, rhenium oxides and tungsten oxides. Oxides such as iron oxide are being used in proplnts as a combustion catalyst. A report on the efforts to correlate composite proplnt burn rate, AP particle size distribution and ferric oxide specific surface and levels, has been proposed by Burnside (Ref 56). Two proplnt comnps were used: viz, (1) hydroxy-terminated polybutadiene based proplnts (HTPB) consisting of HTPB binder 11.6, polyamine/epoxide binding agent 0.4, AP 77.6−76.0, aluminum (15 micron) 10.0, and ferric oxide 0.4−2.0%; and (2) carboxy-terminated polybutadiene based proplnts (CTPB) consisting of CTPB binder 14.0, AP 80.0−80.9, aluminum (5 micron) 5.0, and ferric oxide 0.1−1.0%. The experiment was conducted using these proplnts contg ferric oxide of 3 to 2.64M²/g surface area in lab scale motor firings. Results indicate that Fe₂O₃ specific surface is more significant at
high, 7–11 micron size AP levels than at low, 7–11 micron size AP levels. It was also concluded that catalysis probably takes place in the primary diffusion flame located at the AP binder interface. Inorganic oxides have been used as anti-fouling or anti-barrel wear additives for years. One of the early inventions, that of Hennig (Ref 2), used 1–5% tin or lead oxides (or carbonates) as additives to NC propellants to prevent gun fouling. A number of other patents which are described in this Vol under Propellants, Solid also recommend the use of inorganic oxides, among other additives to propellants, to reduce gun barrel wear or erosion. The oxides used include: MgO, TiO₂, Sr₂O₃, ZnO, BaO, Sb₂O₃, Ta₂O₅, WO₃, U₂O₅ and HfO₂. Also, according to Phené (Ref 50) a similar effect is obtd by the addn of 1% MoO₃ to 7.62mm cast proplnt. Aside from barrel erosion considerations, fluorocarbon composite propellant burning rates, pressure exponents, and temp coefficients of burning rates can be adjusted by the addn of magnesium, copper and manganese oxides. Also, a technique which is used to suppress unstable burning in polyurethane, nitropolyurethane, polyesteracrylate and rubber-base composite propellants is the addn of finely divided oxides of Al, Zr, Si, Th, Ti, or La (Ref: see under Propellants, Solid in this Vol)

In Pyrotechnics military ord has found the greatest use for inorganic oxides. They are either incorporated initially in the compn or formed during the combustion phase of the pyrot, emitting both heat and light in the process. According to Schladt (Ref 3), oxides of metals such as iron, lead and silicon are reduced by aluminum and magnesium upon ignition to evolve intense light. A typical compn includes iron oxide 41.0, barium nitrate 33.5, and magnesium 25.5%. Another use of oxides reported by Schladt (Refs 4 & 5) is in the development of a compn for white smoke puff ground troop signals (rifle signal). This smoke compn (called SP-1) included red phosphorus 50.0, willow charcoal 40.0 and zinc oxide 10.0%. It was found satisfactory and recommended for use. Zinc oxide has also been used as a smoke charge when loaded into 3" antiaircraft shell (Ref 8). Similarly, yellow smoke compns have been created using As₂O₃ and powdered glass (SiO₂) (Ref 2a). According to Eppig (Ref 9) a T-15 airport flare compn containing titanium dioxide was developed which generates 400,000 candlepower. Again, Eppig (Ref 10) reports the use of titanium dioxide as the chief oxidant in a smokeless illuminant compn for the T-24 flare. Of course the role of the inorganic oxide in pyrots has been investigated to determine its effect on heat of reaction, temp, enthalpy, etc. One such investigation has been conducted by Lipscomb (Ref 52a) into the effects of prepn temp, selected impurities, and mechanical activation of ferric oxide on the pyrot properties of the reaction Fe₂O₃ + 3Ti = 3TiO + 2Fe. Another such investigation by Lipscomb (Ref 54) concerns lead monoxide in its reaction with silicon while both are doped with varying amounts of lithium and chromium. It was found that these impurities effected the enthalpy of the reaction Pb + Si = SiO + Pb drastically, changing activation energies and reaction kinetics. Still another investigation by Kirshenbaum et al (Ref 49) examined the flare performance of the gaseous system H₂ + O₂ + BF₃ resulting in BO₂ + HF + BO. It was concluded that the performance of gaseous systems are quite comparable to solid flare systems and that visible emission is in the main from excited BO₂. Of the many pyrots which have been patented, more than several use inorganic oxides. An igniter compn for tracer projectiles devised by Clay and Sahlin (Ref 17) is of interest. This compn replaced magnesium with Ca silicide as the fuel resulting in a dim or invisible trace to a minimum distance of 25 yds and a bright and properly colored trace at greater distances. A typical igniter compn consisted of SrO₂ 78.0, BaO₂ 4.0, PbO₂ 4.0, Ca silicide 7.0 and Ca resinate 7.0%. In two other inventions of Heiskell (Ref 18), dark-burning, non flash pyrot igniter mixts were devised consisting in one compn of CuO 50.0, Mn 49.0 and graphite or stearic acid to act as a binder and lubricant 1.0%; and in another compn of BaO₂ 80.0 and Cr₂0 20.0%. Other possible O₂—bearing compnds described included BaO₂, Sb₂O₅, and PbO₂. In still another invention, that of DeMent (Ref 28), various colored smokes are generated using inorganic oxides. For example a grey smoke consists of As₂O₃ 1, NaClO₃ 4, dextrin 3, and trichloroacetic acid 1.8 parts. More than 370 formulations are described, many using germanium dioxide, boron
tri oxide, and/or titanium dioxide. The inventor suggests uses in military signaling, movement screening, and toxic or radioactive aerosol dissemination. A patent by MacDonald (Ref 36) describes a pyrot compn contg ferric oxide and finely divided SrO₂. This incendiary compn is obtd by initially melting 240 parts of aluminum with 715 parts of Fe₂O₃ plus 30 parts of SiO₂ at 840-1000°C for 10-15 mins. The RT compn produces intense heat when ignited in air. In a patent by Dede et al (Ref 39) lower metal oxides are used to obtn ignition mixes of decreased combustion temp. Thus, Cu₃O 63.6 and KClO₃ 36.4% are homogenized and granulated to 50 micron, then mixed with 0.5 part of a 2% tylose soln, rehomogenized and regranulated to 100-500 micron, and dried at 60°C to 1% w content. In another patent, that of Perkins et al (Ref 46), a non corrosive igniter was developed with a display functioning reliability increase of from a base of 50-60% to 75-80%. The compn includes PbO₂ oxidizer 65-70, Zr fuel (20-100 micron) and stabilized red P 2-6%, and, because of its greater display functioning reliability, it is used with corrosive tracer compns in smaller than usual tracer cavities within the progs so that premature ignition and resultant barrel corrosion is prevented. In the invention of Helms and Rozner (Ref 52), inorganic oxides are used in a pyrot compn to provide a jet of molten material thru a torch nozzle while under the press generated by N₂ or an inert gas, or gasification of a substance such as polytetrafluoroethylene, which is included in the hot reaction mixtu. The compns used in the invention generate large amts of heat at a controlled rate in the readily useable form of a hot gas driven molten jet. In one version of the invention the pyrot compn consists of a finely divided mixt of Ni 5-50, a metal oxide such as Fe₂O₃, Fe₃O₄, and/or Cr₂O₃ 20-76, plus Al (or a mixt of Al with Mg, Zr, Bi, Be or B in 1 to 1 ratio) 15-50%, all contained in the gas source, ready to be sprayed out upon ignition. One of the latest inventions employing inorganic oxides is that of Lipscomb and Smith (Ref 53). In this invention the heat of combustion (Q₀) of Fe₂O₃ or ZnO is increased approx 50% (see table below) by soln of a metallic salt such as Fe₂(SO₄)₃ or ZnSO₄ in boiling w contg 1-5% of a Li or Zr doping compd, then evapg to a paste and calcining at 600-1000°C, yielding doped oxide agglomerates of 0.5-1 micron particle size.

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<td>760</td>
</tr>
<tr>
<td>Zr</td>
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<tr>
<td>Li</td>
<td>5.0</td>
<td>1100</td>
</tr>
</tbody>
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The Following are Selected Inorganic Oxide Entries:

Aluminum Oxide (Alumina, &Alumina, Corundum, Alandum). Al2O3, mw 101.96, v hard white crystal powd, mp 2045°, bp 2980°, d 3.965g/cc. Insol in w, v sl sol in aq alkaline solns. Found in nature as a mineral such as bauxite. Lab prep is by heating aluminum hydroxide to above 1100°. It is used as a chemical reagent, as a smoke and flash reducer and storage stabilizer in NC base proplnts, in rubber-base composite proplnts as discussed above, and in pyrot compns.

The USA Military Specification (Ref 2) contains the following requirements and criteria: (1) form and color; white powder, (2) date of mfg; not older than one year, (3) chloride as AgCl turbidity; 0.01% max, (4) silicates as insol matter after KH2SO4 fusion; trace max, (5) sulfate as BaSO4 turbidity; 0.07% max, (6) alkalies and alkaline earths gravimetrically as the sulfate; 0.50% max, (7) heavy metals as PbS turbidity; 0.007% max, (8) Fe as a Fe(CNS)3.9K2O.4H2O red coloration; 0.015% max, (9) H2O as wt loss on ignition; 5.00% max and (10) w sol substances det by wt loss; 0.75% max.

High concns of aluminum oxide dust can cause various types of lung damage such as Shaver's disease, fibrosis, emphysema and pneumothorax.

Arsenic Pentoxide (Arsenic Acid Anhydride, Arsenic Oxide). As2O5, mw 229.84, white amorph powd, mp 315° (decomp.), d 4.32g/cc. Sol in alc, acids, alkalies and w. Prep is by heating a mixt of As2O3 with concd HNO3 (d 1.38g/cc) until the evl of nitrogen oxides ceases. The soln of H2AsO4 is then evapd to dryness, redissolved in w and reevapd until a temp of over 300° is reached. It is used as a chemical reagent.

The USA Military Specification (Ref 8) contains the following chemical criteria and requirements: (1) As2O5 by sodium thiosulfate–iodine titration; 99.0% min, (2) As2O3 by carbonate–iodine titration; 0.05% max, (3) Cl as AgCl turbidity; 0.005% max, (4) heavy metals as PbS turbidity; 0.010% max, (5) Fe as a Fe(CNS)3.9K2O.4H2O red coloration; 0.010% max and (6) nitrate as an indigo carmen blue coloration which persists for over 5 mins.

Poisonous! LD50 lethal dose to 50% of the animals tested) 8mg/kg


Arsenic Trioxide (Arsenous Acid, Arsenous Acid Anhydride, Arsenious Oxide, Arsenic Sesquioxide, White Arsenic). As2O3, mw 197.82;
white, amorph, glassy lumps; mp 313°, d 4.32 g/cc. Sol in HCl, alk, alk carbonate and w. Prepn is by heating arsenical pyrite ore in oxygen to produce crude As₂O₃ (Ref 4). Pure As₂O₃ is obtd by reacting crude As₂O₃ with HCl and dist of AsCl₃. Any SbCl₃ is removed from the distillate by shaking with concd HCl. The pure AsCl₃ is then hydrolyzed in agitated boiling w, and pure As₂O₃ crystallizes out on cooling. It is used as a chemical reagent and for evolving smoke in pyrots (see above).

The USA Military Specification (Ref 10) contains the following requirements and criteria:
(1) appearance; white powd, (2) As₂O₃ by sodium carbonate–iodine titration; 98.0% min and (3) moisture by wt loss after oven drying; 0.10% max

**Poisonous!** LD₅₀ orally in rats: 138mg/kg

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9) Sax (1968), 438
11) ChemRubHdb (1975), B-69

**Barium Oxide** (Barium Monoxide, Baruya, Barium Protoxide, Calcined Baruya). BaO, mw 153.36; colorl or white to yelsh-white deliq powd; mp 192³, bp 2000°, d 5.72g/cc. Sol in dil acids, ethanol, methanol and w (decomps with a large amt of heat being evolved). Prepn is by thermal decomp of BaCO₃ under high vacuum. It is a product of the burning of the many barium comps present in pyrots and, as discussed above, it is used as an anti-barrel wear additive in propellant comps.

No USA Military Specification exists for this compd

**Poisonous!** Max Allowable Conc for an 8 hr day, 0.5mg/cm² of air

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**Beryllium Oxide** (Bromellite). BeO, mw 25.01, white amorph powd, mp 2530°, bp ca 3900°, d 3.01g/cc. Sol in concd acids and alkalies. V sl sol in w. Prepn is by burning BeCO₃ at 900° in a Pt crucible to the oxide. It is used in nuclear reactor fuels and moderators as well as in powder metallurgy, ceramics, fuel cells and coatings (see above)

No USA Military Specification exists for this compd

**Extremely poisonous!** V small concns are fatal after brief exposure

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**Bismuth Trioxide.** See Vol 2, B162-R

**Boron Oxide.** See Vol 2, B252-L to B253-L

**The Bromine Oxides.** See Vol 2, B306-L to B307-L
Cadmium Oxide. CdO, mw 128.41, dk brn infusible powd, mp 900° (decomps), bp subl 1550°, d 8.15g/cc. Insol in w and alk, sol in dil acids and amm hydroxide. Coml prepns is by reacting Cd metal with air during distn, and collecting the oxide in a baghouse. Lab prepns consists of burning the carbonate in air. It is used as a chemical reagent.

The USA Military Specification (Ref 4) contains the following requirements and criteria: (1) cadmium by ethylendiaminetetraacetiac acid titration; 87.0% min, (2) silver, lead, tin, copper, mercury, zinc and iron by either atomic absorption or emission spectrographic techniques; total 0.050% max, (3) arsenic, antimony and thallium to be detd as in "(2)"; 0.005% max, (4) volatiles by wt loss after oven drying; 0.50% max, and (5) appearance; reddish-brown powd.

Poisonous! Human tolerance, 0.1mg/cc of air.


Calcium Oxide (Lime, Quicklime, Burnt Lime, CaO, Unslaked Lime, Fluxing Lime). CaO, mw 56.08, white or greyish-white lumps or powd, mp 2580°, bp 2850°, d 3.25–3.40g/cc. Sl sol in w with formation of calcium hydroxide and evolution of large amts of heat; sol in acids, and insol in ethanol. Coml prepns consists of heating carbonate in kilns at 1000–1100° until all of the CO₂ is driven off. Lab prepns is by burning calcium carbonate or calcium oxalate at about 800° using a quartz crucible in an electric furnace.

The USA Military Specification (Ref 5) contains the following requirements and criteria for Grade A (bleaching grade) and Grade B (fluxing grade): (1) nonvolatile matter by wt loss after ignition in an electric furnace: Grade A, 94.0% min and Grade B, 98.0% min, (2) calcium oxide by gravimetric procedure (Ref 9): Grade A, 90.0% min and Grade B, 95.0% min, (3) magnesium oxide by gravimetric procedure as magnesium pyrophosphate (Ref 9); Grade B, 1% max, (4) iron and aluminum oxides by gravimetric procedure (Ref 9), Grade B, 1.0% max, (5) silicon dioxide by loss in wt after electric furnace ignition, Grade B, 1.0% max, (4) iron and aluminum oxides by gravimetric procedure (Ref 9), Grade B, 1.0% max, (5) silicon dioxide by loss in wt after electric furnace ignition, Grade B, 1.0% max, and (6) particle size by retention on individual members of a set of US Standard Sieves after agitation on a mechanical shaker — 1.5 sq inch (37.5mm) openings, Grade A – 1.0% max; 1 sq inch (25.0mm) openings, Grade A – 7.0% max; 1/8 inch round (3.2mm round) openings, Grade A – 95.0% min; No 3 (0.223 inch) openings, Grade B – 0.0% max, and No 12 (0.0661 inch) openings, Grade B – 95.0% min.

A strong caustic irritant. Dangerous near organic materials. Tolerance, 5mg/cc of air.

Besides its use in pyrocs, calcium oxide has been used in a number of expl devices such as Jarolimek’s igniter, Elliott’s “Quicklime Explosive”, and the various cartridges of Smith and Moore, Arnould, and Steinau (Ref 1). All of these are presented in greater depth above, together with the current usage of the oxide.


Ceric Oxide (Cerium Dioxide, Cerium Oxide, Ceria). CeO₂, mw 172.13, white powd, mp ca 2600°, d 7.132g/cc at 25°. Sol in concd sulfuric and nitric acids, insol in dil acids and w. Prepns is by dissolving CeCO₃ in 16N HNO₃ contg 3% H₂O₂ and then evap off the nitrate soln followed by thermal decompn. The yield is 97.6% of 99.8% pure CeO₂. The oxide is used in optics, electronics, as a diluent in nuclear fuels (as
above), for fueling gas-generating propulsion units and as an anti barrel wear additive to propellants.

There is no USA Military Specification for this compd


The Chlorine Oxides. See Vol 3, C243-L to C244-R

Chromic Acid. See Vol 3, C298-R to C299-L

Chromic Oxide. See Vol 3, C299-R

The Copper Oxides. See Vol 3, C522-R to C523-L

The Iron Oxides. See Vol 6, F15-L to F17-L

The Lead Oxides. See Vol 7, L9-L to L10-L

Magnesium Oxide. See under Magnesium, M9-L in this Vol

The Manganese Oxides. See under Manganese, M12-L & R in this Vol

Molybdenum Trioxide (Molybdenum Anhydride, Molybdc Oxide, Molybdic Acid Anhydride). MoO₃, mw 143.95, white powd, mp 795°, bp 1155°, d 4.696g/cc at 26/4°. Sl sol in w, sol in acids, alk sulfates and amm hydroxide. Prepn is by first boiling concd nitric acid with NH₄

molybdate to ppt H₂MnO₄. By dehydration at 150° the H₂MnO₄ is then converted to MoO₃. The trioxide is subseq purified by subln in a quartz tube at 780°. The trioxide is used in igniter compns and proplnt compns (see above)

The USA Military Specification (Ref 8) contains the following requirements and criteria: (1) molybdenum trioxide gravimetrically as lead molybdate; 99.5% min, (2) insoluble in dil amm hydroxide as loss in wt; 0.010% max, (3) chloride as silver chloride turbidity; 0.002% max, (4) nitrate as an indigo carmen blue coloration which persists for over five mins; 0.003% max, (5) arsenate, phosphate and silicate (as SiO₄) as a blue coloration in acidified 4-methyl-2-pentanone which should not exceed that in a control; 0.001% max, (6) sulfate as barium sulfate turbidity which should not exceed that of a standard; 0.020% max, (7) ammonium colorimetrically with Nessler’s reagent; 0.002% max, (8) lead as PbS colorimetrically; 0.005% max, (9) average particle size using the Fisher Sub Sieve Sizer (Ref 3); 8 ± 4 microns and (10) workmanship by inspection — material to be free flowing and free of lumps, dirt, chips or other foreign mat

The trioxide has a low toxicity; max acceptable tolerance level is 5mg/cc of air (human) and I.D₇₅ intraperitoneal (ip) in guinea pigs is 400mg/kg


Nitrogen Oxides. See in this Vol, N129-L to N133-L
Potassium Oxide (Potassium Monoxide). K₂O, mw 94.20, white, loose, deliq powd, mp 350° (decompn), d 2.32g/cc at 0°. Reacts with w very readily to form KOH with evoln of 75 kcal/mole. V sol in w, sl sol in ethanol and eth. Prepn is by mildly heating carefully purified K in the presence of pure dry air. Excess K is distd off at 350° under high vacuum. The K₂O is 99.5% pure. Also produced when K compds are burned in pyrots

No USA Military Specification exists for this compd

The oxide is highly caustic and corrosive, and is a moderate fire hazard


Silicon Dioxide (Quartz, Lechatelierite, Tridymite, Silica, Silicic Anhydride, Rock Crystal, Cristobalite, Sand). SiO₂, mw 60.08, Sol in HF, v sl sol in alk and insol in w and acids. Found so widely in nature that no mfg or lab procedures are usually needed for impure mat. It is a product resulting from burning Si or Si compds in pyrots. Pure SiO₂ can be prep’d in several ways: (1) the transparent or fused variety is manuf’d by vapzn of sand at 3000° in an electric arc furnace, and (2) amorph SiO₂ is obt’d as a fine white powd by decompg pure SiCl₄ with w and heating the resulting gel. Its uses (see above) are in detonators, thixotropic control in the manuf of aerial mine expl charges, micromines (Gravel), anti barrel wear additives to propnts, flares, in cast form as radomes, as well as in such uses as paints, cements, etc

<table>
<thead>
<tr>
<th>Allotropic Form</th>
<th>Appearance or Crystal Form</th>
<th>Mp, °C</th>
<th>Bp, °C</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>cristobalite</td>
<td>color, cub or tetragonal</td>
<td>1710</td>
<td>2230</td>
<td>2.32</td>
</tr>
<tr>
<td>lechatelierite</td>
<td>color, amorph, vitreous</td>
<td>—</td>
<td>2230</td>
<td>2.20</td>
</tr>
<tr>
<td>quartz</td>
<td>hex</td>
<td>1610</td>
<td>2230</td>
<td>2.653—.66</td>
</tr>
<tr>
<td>tridymite</td>
<td>rhombic</td>
<td>1703</td>
<td>2230</td>
<td>2.28—.33</td>
</tr>
</tbody>
</table>

There are two USA Military Specifications for the use of silica in ammo (Refs 3 & 4). Ref 3 contains the following requirements and criteria for special purpose silica Type I (alkaline), Type II (acid), and Type III (hydrophobic):
<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area, m²/g&lt;sup&gt;a&lt;/sup&gt;</td>
<td>300 ± 50</td>
<td>325 ± 50</td>
<td>130 ± 25</td>
</tr>
<tr>
<td>Ignition loss, %&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.0 ± 2.0</td>
<td>11.0 ± 2.0</td>
<td>7.5 ± 2.5</td>
</tr>
<tr>
<td>Loss at 105°, %&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6.0 max</td>
<td>6.0 max</td>
<td>4.0 max</td>
</tr>
<tr>
<td>HF Residue Test, %&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.0 max</td>
<td>3.0 max</td>
<td>3.0 max</td>
</tr>
<tr>
<td>pH&lt;sup&gt;e&lt;/sup&gt;</td>
<td>8.5 ± 0.5</td>
<td>5.0 ± 0.5</td>
<td>5.0 ± 0.5</td>
</tr>
<tr>
<td>No 325 (44 microns) mesh wet sieve residue, %&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.02 max</td>
<td>0.02 max</td>
<td>NA</td>
</tr>
<tr>
<td>Water repellency, %&lt;sup&gt;g&lt;/sup&gt;</td>
<td>NA</td>
<td>NA</td>
<td>99.5 min</td>
</tr>
<tr>
<td>Viscosity, cps at 25°&lt;sup&gt;h&lt;/sup&gt;</td>
<td>NA</td>
<td>NA</td>
<td>2000 ± 500</td>
</tr>
</tbody>
</table>

NA — not applicable

a — as the BET (Brunauer, Emmett and Teller) value

b — as the wt loss.

c — as the wt loss

d — as the wt loss on ignition

e — as the pH meter reading of a glass electrode vs a calomel std electrode

f — as the wt of the residue

g — as the residue miscible with water

h — as the Brookfield Viscometer measurement

Ref 4 contains the following requirements and criteria for silica: (1) finely divided similar to “Cab-O-Sil”, Grade M-5, made by the Cabot Corp of Boston, Mass, (2) surface area as ml of NaOH titrant used to achieve a pH of 9.0; 175 to 225m²/g, (3) density as the wt of a known vol of silica; 2.3 lbs/cu ft max, (4) moisture as loss in wt; 1.5% max, (5) pH as the measurement made using a Beckman Model G pH Meter with glass vs calomel electrodes; 3.5 min to 4.2 max and (6) suspension as miscibility with fluoroethane after agitation; no settling in 10 mins

Long exposure to SiO₂ dust can result in fibrosis of the lung or silicosis which may eventuate in pulmonary hypertension and cor pulmonale. Susceptibility to tuberculosis is enhanced. The tolerance level for crystall forms of SiO₂ is calculated from the formula 250/ (%SiO₂+5), and for amorphous forms the tolerance level is 20 millions of particles/cu ft of air


Silicon Monoxide. SiO, mw 44.09, hard and abrasive, black to brn-black amorph or cubic crysts, mp > 1702°, bp 1880°, d 2.13–20. Sol in concd aq alk and dil HF+HNO₃. Prepn is by subliming finely divided silicon at 1250° under high vacuum for 4 hrs. It is used as a coating for precision optical lenses

The USA Military Specification (Ref 14) contains the following requirements and criteria: (1) a pre-production sample must meet the Spec requirements, (2) silicon monoxide shall be of a high purity grade, (3) chemical compn as detd by the powder—D-C arc semiquantitative technique
of spectrochemical analysis (ASTM E-2 SM 11-2) for: a) iron; 0.01 to 0.10%, b) nickel; 0.02% max, c) aluminum; 0.01 to 0.05%, d) molybdenum; 0.01% max, e) copper; 0.01 to 0.10%, f) manganese; 0.01 to 0.10%, g) magnesium; 0.01 to 0.05%, h) titanium; 0.02% max, i) boron; not detected, j) chromium; 0.03 max, k) free silicon; 0.10% max, l) silicon monoxide; 95.0% min, and (4) workmanship of such a level as to assure a uniform product in Spec compliance.

Silicon monoxide has the same toxicity as the dioxide.


Sodium Oxide (Sodium Monoxide). Na₂O, mw 61.98, white-grey deliq powd, mp 1275° (subl), d 2.27/g/cc. Combines violently with w, forming NaOH. Sol in w and ethanol with decomp. Reacts with acids to neutralize them. Prepn is by reacting NaOH with Na in a nickel crucible at 320° under high vacuum. Yield is 96%. The oxide is stored under anhyd benz. It is also the product of the ignition of many of the sodium comds found in pyrots. It is used as a chemical reagent for organic polymerization or condensation reactions.

No USA Military Specification exists for this compd. The oxide is extremely corrosive and should be handled with tongs! Max allowable concn (MAC) is 2mgs/m³ of air.


Stannic Oxide (White Tin Oxide, Tin Dioxide, Stannic Anhydride, Flowers of Tin, Stannic Acid, Cassiterite). SnO₂, mw 150.69, white powd, mp 1127°, bp 1800–1900° (subl), d 6.95 g/cc. Sol in concd sulfuric and concd hydrochloric acids, sol in hot concd aq KOH or NaOH. Prep is by reacting Sn with concd nitric acid (d 1.41 g/cc) on a w bath forming β-stannic acid. The β-stannic acid is then heated to a red heat and converted to SnO₂. It is used as a chemical reagent and (see above) as an antifouling, flash and barrel wear reducing additive in propmts.

The USA Military Specification (Ref 7) contains the following requirements and criteria: (1) material as a fine white cryt powd by inspn, (2) volatile content as wt loss on oven drying at 110°; 0.50% max, (3) stannic oxide as SnCl₂ by by iodometric titration to a blue (starch) end point; 98.20% min, (4) Class 1 and 2 types of granulation as the wt of oven-dried (at 105°) material passed thru a sieve when a w-ethanol suspension is w-washed thru a No 200 (74 micron) sieve, Class 1 – 95% min and Class 2 – 95% min; and then, using another sample, thru a No 325 (44 micron) sieve, Class 1 – 85% and Class 2 – 90% min; and (5) acidity as sulfuric acid using NaOH titrant to a methyl red end pt; 0.01% max

The oxide can cause relatively benign pneumoconiosis.

Titanium Dioxide (Titania, Titanium White, Rutile, Anatase, Brookite, Titanc Anhydride, Titanc Acid Anhydride, Titanc Oxide). TiO₂, mw 79.90;
Selected Parameters of the Allotropic Forms of TiO₂

<table>
<thead>
<tr>
<th>Allotropic Form</th>
<th>Appearance or Cryst Form</th>
<th>mp, °</th>
<th>bp, °</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>brookite</td>
<td>white, rhomb</td>
<td>1825</td>
<td>-</td>
<td>4.17</td>
</tr>
<tr>
<td>rutile</td>
<td>col, tetr</td>
<td>1830–50</td>
<td>2500–3000</td>
<td>4.26</td>
</tr>
<tr>
<td>anatase</td>
<td>brn-blk, octahedrite</td>
<td>-</td>
<td>-</td>
<td>3.84</td>
</tr>
</tbody>
</table>

Sol in hot concd sulfuric acid, HF and alk. The dioxide occurs in nature as limonite (FeO, TiO₂) or rutile. Cornprepn is by extrn of the ore with concd sulfuric acid, followed by heating, filtering, washing and then calcining at 800–1000⁰ to produce anhydrt TiO₂. Labprepn is by mixing a cold soln ofaq TiCl₄ with a cold HCl buffered soln of concd (NH₄)₂SO₄ and then bringing the combined solns to a boil while adjusting the pH to 1.0 using ammonia. The resulting ppt is then dried at 107⁰, calcined for 1 hr at 800⁰, ground and washed. Recalcining at 1000⁰ yields a rutile with 99.8% TiO₂ content. The dioxide is also a prod of the combn of Ti used in pyrots. It is used as an anti barrel wear additive in proplnts, a pyrot smoke generator, a smoke inhibitor in pyrots, and a propn burning-rate modifier (see above). It is also used as a paint pigment of great hiding power, when combined with wax it becomes an additive liner for artillery carts, and, in the form of single cryts, as high temp transducers having microsec response.

The USA Military Specification (Ref 13) contains the following requirements and criteria:
(1) titanium dioxide as the titanous reduced ferrous salt by KMnO₄ titration; 98.0% min, (2) coarse particles retained on a No 325 (44 micron) sieve after w washing and brushing; 0.25% max, (3) specific gravity as the wt of kerosene displaced in a pycnometer; 3.8 to 4.2 g/cc at 15.6⁰, (4) oil absorption as the wt of raw linseed oil used when incorporated by rubbing on a glass plate with TiO₂ using a steel spatula; 20.0 to 40.0 lbs/100 lbs TiO₂, (5) water solubility as the wt of mat recovered by filtn of an aliquot of a boiling w digestion of a sample of the oxide; 0.2% max, (6) hydrogen ion concn as pH using a glass vs calomel electrode; 7.0 to 8.0, (7) moisture by loss in wt after oven drying at 105–110⁰ for 2 hrs; 0.7%, (8) compatibility as detd using M30 propn in a 50/50 mixt when heated at 100⁰ for 40 hrs at a press of 5mm; 3ml of gas max, and (9) first article inspection as specified in the delivery contract.

The dioxide is considered a nonhazardous respiratory nuisance with a tolerance value for dust 15mg/ m³ of air.


Tungsten Dioxide. WO₂, mw 215.92, brn cubic cryts or amorph powd, mp 1851.60⁰ (decomp with ign in air), 1500–1600⁰ (decomp with ign in N), bp ca 1430⁰ (subl at 800²), d 12.11g/cc. Sol in acids andaq KOH. Prepn is by heating a mixt of WO₃ and W in a sealed evacuated quartz tube at 950⁰ for 40 hrs. The amorph powd is strongly pyrophoric and is easily oxidized to WO₃.

No USA Military Specification exists for this compd.

The dioxide is a toxic upon heavy ingestion (over 10% of the diet) and by dust inhalation to expdl animals.

Xenon Trioxide. \( \text{XeO}_3 \), mw 179.30, colorless crystal, trig pyramidal, hygroscopic, mp 30–40\(^\circ\) (explosive). V sol in w. Prep (with care) by reacting xenon tetra- or hexafluoride with \( \text{Xe} \) at RT under partial vacuum. The compd is stable at RT in aq soln. It explds when dry and is rubbed, pressed, or gently heated. A RH of over 20\% decreases the stability of the dry compd. No USA Military Specification exists for this compd.

The aq soln is a strong oxidizing agent and a strong irritant. The compd is highly toxic by inhalation.


Xenon Tetroxide. \( \text{XeO}_4 \), mw 195.30, colorless gas, mp –40\(^\circ\) (explosive). Prep is by reacting sodium perxenate with concd sulfuric acid. Compd is unstable.

No USA Military Specification exists for this compd.


Zinc Oxide (Flowers of Zinc, Zinc White, Zinc Bloom, Philosopher’s Wool, Chinese White, Zincite). \( \text{ZnO} \), mw 81.38, white or yellowish-white amorphous odorless powd with a bitter taste, mp 1975\(^\circ\) (subl and decomp), d 5.47–5.606 g/cc. V sl sol in w, sol in mineral acids, dil acet acid and \( \text{NH}_3 \). Comp is prep from Zn or ores such as Franklinite or Zinc Blende by vapzn in a CO atm with subsequent oxidation of the vapors with preheated air. Lab prep is by converting anhyd zinc oxalate to \( \text{ZnO} \) by heating at 400\(^\circ\) for 4 hrs. It is also a product of the burning of Zn in pyrots. Zinc oxide is used as a caking (or setting) inhibitor for \( \text{AN} \) (explosives) compns, an anti-barrel wear additive in proplns, and an ingredient of smoke generating pyrot compns.

The USA Military Specification (Ref 7) contains the following requirements and criteria for Grade A (pyrotechnic mix) and Grade B (stabilizer for XXCC3 impregnate): (1) zinc oxide by titration with a std soln of K ferrocyanide; Grade A – 98.5\% min and Grade B – 99.0\% min, (2) water-soluble salts as loss in sample wt; Grade A – 0.50\% max and Grade B – 0.50\% max, (3) sulfur (as SO\(_3\)) gravimetrically as BaSO\(_4\); Grade A – 0.40\% max and Grade B – 0.10\% max, (4) lead oxide (as PbO) gravimetrically; Grade A – 0.60\% max and Grade B – 0.10\% max, (5) loss in wt at 110\(^\circ\); Grade A - 0.30\% max and Grade B - 0.50\% max, (6) cadmium (as CdO) gravimetrically as CdS; Grade A – 0.20\% max, (7) arsenic (as As\(_2\)O\(_3\)) gravimetrically as As sulfide; Grade A – 0.10\% max, (8) antimony (as Sb\(_2\)O\(_3\)) gravimetrically as Sb sulfide; Grade A – 0.10\% max, (9) particle size – as Class 1 (regular grind for both Grade A and Grade B), 99.9\% min by (dry) wt shall pass thru US Std Sieve No 140 (105 microns) and 99.0\% min thru sieve No 170 (88 microns); and Class 2 (fine grind for Grade A only), average particle size using the Fisher Sub Sieve Sizer (Ref 2a); 5.0 microns max, (10) moisture reabsorption by wt difference; Grade A – 0.15 to 0.54\% min and max, and (11) apparent density by pycnometer; Grade A (Class 1) – 0.75g/cc min.

Vaporized zinc oxide is sol to moderately toxic on inhalation and can cause “brassfounders ague” or “brass chills”. MAC for an 8 hr working day is 15mg/m\(^3\) of air. It is an eye irritant.

Oxidized Rosin (Résidéee in Fr). An exp1 material, prepd by E. Steele of Engl by treating a mixt of 90 parts of colophony (rosin) and 10p of starch with 67% nitric acid (42°Be). After washing, drying, and powdering, the résidéee was moistened with methylol, mixed with K chloride (sometimes with other ingredients), and then warmed gently with stirring to evaporate the methylol. The resulting mixts were the so-called "Steel-ites" (qv), mining expls used in Fr and Engl during the early part of this century
Ref: Davis (1943), 360

Oxinite (Oxinita in Spanish). An exp1 mixt of Nitroglycerol and Dinitrodiglycol prepd by Ohman in Sweden in 1936 directly from ethylene by an electrolytic method.

The electrolytic bath consists of two compartments, anodic and cathodic. In the first, Pt gauze is immersed in an acet soln of Ca nitrate which is kept constantly saturated with ethylene, by bubbling ethylene thru it in such a manner that it sweeps over the surface of the Pt gauze. In the cathodic compartment, Al is immersed in a soln of Ca nitrate in nitric acid. The level of the liq in the cathodic compartment is maintained above that of the anodic, and the liq moves from the first to the second compartment as the electrolysis progresses. The discharge of the nitrate ion (NO₃⁻) at the Pt gauze anode liberates the free nitrate radical (NO₃), which reacts with ethylene, with the formation of Nitroglycerol and Dinitrodiglycol;

1) CH₂=CH₂+2NO₃⁻ → CH₂(O.NO₂)₂.CH₂(O.NO₂),
and 2) 2CH₂=CH₂+2NO₃⁻+[O] → CH₂(O.NO₂).CH₂-OH₂CH₂.CH₂(O.NO₂)

In the second reaction, the oxygen is supposed to be obtained as a result of the following side reaction; (NO₃)₃+NO₃⁻ → N₂O₃+[O]

After the electrolysis is completed, the cathode soln is fortified with nitric acid for reuse, while the anodic liq is neutralized with slaked lime and distd in vacuo to recover the acet. The residue contains Ca nitrate and a mixt of Nitroglycol and Dinitrodiglycol. After removal of the Ca nitrate, the mixt of expls is water washed and dried.

This mixt, called "Oxinite", contains up to 15.9% N, and has been proposed for use in low-freezing Dynamites as a substitute for NG (See also under "Electrochemical Nitratons" in Vol 5 E61-1).

Oxland Powder. An exp1 patented in 1860 in Engl, prepd by substituting Na nitrate for a part of the K nitrate in BlkPdr
Ref: Daniel (1902), 593

Oxonite (Oxamite). Brit Sprengel type expl (see Vol 6, E364-R) invented in 1883 by Punchon and Vizer. It consisted of a cotton bag (cartridge) filled with powdered Picric Acid (PA), inside of which was a glass tube filled with fuming nitric acid. This tube was broken at the moment the cartridge was introduced into a borehole, causing the acid to soak into the PA, and resulting in an expln.

The compn of the ingredients varied between 46–58% PA and 54 to 42% fuming nitric acid. Davis (Ref 3) gives the formula PA 58 & nitric acid 42%. According to A. Pérez Ara (Ref 4), the Oxonite proposed by Emmens of New York contained PA 46 & nitric acid 54%. Its expl reaction was given as:

3C₆H₂(NO₂)₃OH+7HNO₃→16CO₂+2CO₂+8H₂O+8N₂

Refs: 1) Daniel (1902), 594–5 2) Cölver (1938), 323 3) Davis (1943), 354 4) A. Pérez Ara (1945), 227

Oxonium Compounds. An addition or double compd of an organic oxide with strong acids or their salts, as, R₂.O.HX (Refs 5 & 7)

Oxonium nitrates have been known since 1835 (Ref 1). They were originally described as
addition comds of aldehydes and ketones with nitric acid (Refs 1 & 2). Reddelein (Ref 4) represented the structure of the compds diagrammatically as \( \mathcal{C} = \mathcal{O} \ldots \text{HONO}_2 \). Hofman et al (Ref 6) recently produced evidence of the oxonium structure of the additive comds, on the basis of infra-red absorption spectra as \( C = \text{OH}^+ \text{NO}_3^- \). The products of addition of nitric acid to ethers also possess the same oxonium structure, \( C = \text{OH}^+ \text{NO}_3^- \).

Hofmann et al (Ref 3) obtained the following compds:
- diethylene glycol monophenyl ether
  \[ \text{CIO}_4\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH} \] (I)
- chlorohydrin monophenyl ether
  \[ \text{CIO}_4\text{CH}_2\text{CHOHCH}_2\text{Cl} \] (II) Compd (I) was obtained by treating ethylene oxide with 60% perchloric acid, and compd (II) by the action of 60% perchloric acid on epichlorohydrin.

Both compds are oils immiscible with w, and according to these investigators, both produce an expel effect greater than NG. They are both readily hydrolyzed by w at RT, or in the presence of atm moisture.


5-Oxy-1,5-Azotetrazole ([5-Oxytetrazolyl-(1)]- [Tetrazolyl-(5)]-Diimide). \( \text{N}_2\text{N}_2\text{N}_2\text{N} \equiv \text{N}_2\text{C} \equiv \text{N} \equiv \text{COH} \equiv \text{HN} \equiv \text{N} \) Can be prep'd by passing \( \text{CO}_2 \) thru 5-diazotetrazole, but because the latter compd is very unstable, Thiele and Marais (Ref 2) preferred to start with its salts, which resulted in salts of 5-Oxy-1,5-azotetrazole:

Sodium salt. \( \text{Na}_2\text{C}_2\text{ON}_1\text{O}_5\text{H}_2\text{O} \), yel leaflets. Can be prep'd by passing \( \text{CO}_2 \) thru a boiling eq soln of the Na salt of 5-diazotetrazole. Explodes violently on heating.

**Ba salt.** \( \text{BaC}_2\text{ON}_1\text{O}_4\text{H}_2\text{O} \), yel crystals, difficulty sol in w. As expl as the Na salt.

**Refs:** 1) Bell 26, 596  2) J. Thiele & J.T. Marais, Ann 273, 150-55 (1893)

**Oxybenzolic Acid, Nitrate Lead Salt (Lead 2,4,6-Trinitro-3-Oxybenzoate, Trinitromethyl-oxybenzoate in Fr).** H. Ficherolle and A. Kovache (Ref) prep'd and characterized this material.

**Prepn.** Dissolve 2.4 g of Pb nitrate in 50 ml w at 90-95°, and add with stirring a concd soln of Na benzoate (prep'd by neutralizing 2 g of benzoic acid with 0.6 g NaOH). Evaporate the mixt on a w bath to a small vol while the liq still remains clear. Cool and add 50 ml of 95% ethanol. This results in a very fine, light yel ppt, which is separated by vacuum filtration. After drying at 50°, analysis gave 41.82% Pb and 3.40% water.

**Action of Heat.** Explodes when brought in contact with flame. The more moisture it contains, the more difficult it is to expl; at 20% moisture level it does not expld. When heated in a liq bath, it expls ca 238°.

**Compatibility.** Mixts of equal amt's of Pb trinitro-m-oxybenzoate with PA, TNT, RDX, PETN, K chlorate, AN or Sb\(_2\)S\(_3\), when stored for 40 days in a dry atm at 50°, did not show any weight variation.

**Compatibility with Metals.** Strips of metals, kept for 40 days in Pb trinitro-m-oxybenzoate contg 3.40% water, lost the following amts in g/cm\(^2\): Cu 5, steel 10, Al 15, Sn 415, Pb 565, and Zn 965. The least corroded metals were Cu, steel and Al.

**Hygroscopicity.** It is hygroscopic. When stored in atms of different RH levels for periods up to 40 days, it absorbed the following % of w:

<table>
<thead>
<tr>
<th>% RH</th>
<th>10 days</th>
<th>20 days</th>
<th>30 days</th>
<th>40 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.44</td>
<td>1.62</td>
<td>2.98</td>
<td>3.30</td>
</tr>
<tr>
<td>90</td>
<td>0.50</td>
<td>2.04</td>
<td>3.16</td>
<td>3.78</td>
</tr>
<tr>
<td>100</td>
<td>0.84</td>
<td>2.74</td>
<td>3.88</td>
<td>4.88</td>
</tr>
</tbody>
</table>

**Impact Sensitivity.** Using a 2 kg wt:

- Height of fall in cm  40 60 80 100
- % Detonations for dry product 14 48 60 78
- % Detonations for product 9 9 6 5
  with 6% water

The sensitivity of the wet product is markedly less.
than that of dry material

**Solubility.** In % at 18°C: water 0.92, ethanol 0.14, methanol 0.31, petr eth 0.53, acet 0.15, pyridine 0.20, benz 0.06, CS₂ 0.05, amyl acetate 0.04, trichloroethylene 0.03, chloroform 0.01, CH₄ 0.01, & eth — insol

**Thermal Stability and Volatility.** No loss of wt when stored for 300 days at 50°C, 150 days at 70°C or 50 days at 90°C

**Uses.** Pb trinitro-m-oxynbenzoate has not found any practical application in the expts field

**Ref:** H. Ficheronnque & A. Kovache, MP 31, 9–10 & 25 (1949)

**Oxy cellulose and Derivatives**

**Oxy celluloses.** Products obtained by treating cellulose with oxidizing agents, such as hypochlorite, permanganate, hydrogen peroxide, 47.5–60% nitric acid, chlorates, persulfates, ozone, chromic acid, bromine water in the presence of Ca carbonate, by the action of strong sunlight or ultra violet rays, by an electrolytic method, etc. The nature of the oxy cellulose depends upon the oxidizing agents used and on the conditions of oxidation. Oxy celluloses should not be confused with the ultimate products of the oxidation of cellulose (see Vol 2, C95-R ff). Although oxy cellulose is not used in te expts industry, it would be advisable to describe it briefly, inasmuch as it is a by-product of the nitration of cellulose (see Vol 2, C100-L ff)

The discovery of oxy cellulose is generally attributed to Witz, who prep'd it in 1883 in connection with an investigation of the bleaching of cotton, and who distinguished it from hydrocellulose (see Vol 7, H213). Prior to this, Kolbe (1868) had shown that linen treated with ozone, produced a modified cellulose, and Jeanmarie (1868) had shown that cotton goods treated with dichromate soln, followed by alkaline treatment, produced a material considerably weaker in strength than the original cotton

The following formulas have been ascribed to oxy celluloses prep'd by various methods:

- KMnO₄ yields (4C₆H₁₀O₄ + C₆H₁₀O₆)
- Bromine yields (8C₆H₁₀O₄ + C₆H₁₀O₆)
- Ca(MnO₄)₂ yields (3C₆H₁₀O₂ + C₆H₁₀O₆)
- KClO₃ yields (3C₆H₁₀O₃ + C₆H₁₀O₆)
- Bleaching powder yields (4C₆H₁₀O₃ + C₆H₁₀O₆)

Oxy celluloses differ from cellulose and hydrocellulose in properties, although there is practically no difference in external appearance among the three. The reduction of Fehling’s soln has long been recognized as a characteristic of oxy cellulose. According to Dorée (Ref 7, p 119), the Cu number for cellulose is 0.28, while for various oxy celluloses it varies between 5.8 and 11. The highest obtained is by the oxidation of cotton with hypochlorite, the lowest for hydrogen peroxide. Oxy cellulose prep'd by KMnO₄ gave a Cu number of 8

Another important characteristic of oxy cellulose is the presence of —COOH groups, which may be detd by measuring the amt of CO₂ evolved when oxy cellulose is distilled with 12% hydrochloric acid. While, according to Marsh & Wool (Ref 6) and Dorée (Ref 7), the amt of —COOH contained in oxy cellulose is between 0.3 and 1.3%, cellulose yields only 0.03% and hydrocellulose 0.04%

There is also a difference in total acidity, as caled by the ml of 0.1N NaOH required per g of material: for oxy celluloses (10.4 to 41.4), for cellulose (1.8), and for hydrocellulose (4.6) (Ref 7, p 119)

Urbanski (Ref 8) states that the properties of oxy cellulose depend on its method of prep. Oxidation in a neutral or acid medium gives a product with definite reducing properties; indicating the presence of aldehyde groups. Oxidation in an alkaline medium gives a product with acidic properties, indicating the presence of carboxylic groups. An oxy cellulose of this kind is distinguished from the other by its capacity of being colored by methylene blue

**Nitrogen Peroxide Oxycellulose** was obtained by Eastman Kodak Co (Ref 3) by the action of NO₂ gas (0.6 to 0.9p) on cellulose at 20°C, or below, for 50 hours. It is claimed that oxidation of the terminal carbon took place. This oxy cellulose is sol in 2% NaOH

The nitration of oxy celluloses yield products which resemble Nitrocelluloses in properties (see below)

Nitrooxyxcellulose. $C_{18}H_{23}O_{16}(NO_{2})_3$, mw 633.39, N 6.64% (theory), 6.48% (found). A white expd substance, prep'd for the first time by Cross, Bevan & Beadle (Refs 2 & 3) by nitration of oxyxcellulose. To obtain this material, they treated the gelatinous product obtained on boiling cellulose with nitric acid, corresponding to the formula $C_{18}H_{26}O_{16}$ (Refs 1 & 3), first with concd nitric to wash it free of w. They then dissolved the anhydr oxyxcellulose in a mix of equal vols of nitric and sulfuric acids. The resulting soln was poured in a thin stream into a large vol of cold w, and flakes were obtained of a substance corresponding approx, after drying at 110°, to the above formula. Cross & Bevan (Ref 1) experienced a violent expn while they were heating nitrooxyxcellulose in a flask, together with FeSO$_4$, as prescribed in Eder’s method [Ber 13, 169 (1880)].

According to Marshall (Ref 4), when dry, powdered oxyxcellulosates were nitrated with a mixed acid contg $H_2SO_4$ 46.22, $HNO_3$ 42.03, $N_2O_4$ 0.25 & $H_2O$ 11.50%, nitrooxyxcellosates contg, on the average, 13% N (12.78 to 13.25) were obtained.

Some of the properties of these products are briefly described on pp 156–59 of Ref 4.

Oxydimercuriacetaldehyde (Hydroxydimercuriacetaldehyde). OHC.C(Hg).HgOH. It is known only in the form of its salts, some of which are expd:

Chloratodimercuriacetaldehyde. OHC.C(Hg).HgOClO$_2$, mw 525.70, colori prisms. Can be prep'd by treating an excess of mercuric oxide in an aq soln of chloric acid with an alc soln of acetaldehyde. It is an extremely sensitive expn of the initiating type, exploding even when shaken under liq (Refs 1 & 3).

Nitratodimercuriacetaldehyde. OHC.C(Hg).HgONO$_2$, mw 504.26, N 2.78%, colori prisms from alc. Can be prep'd by adding an alc soln of acetaldehyde to an aq soln of mercuric nitrate, acidified with nitric acid. Nearly insol in w. Puffs off on heating with evolution of a yellow cloud and Hg (Refs 1, 2 & 3).

Nitritodimercuriacetaldehyde. OHC.C(Hg).HgONO, mw 488.26, N 2.87%, light yel powd. Can be prep'd by passing acetylene thru mercuric nitrate and an excess of K nitrite in 1% nitric acid. When dried, it puffs off, either when rubbed or heated (Refs 1 & 3). 


$1,1^′$-(Oxydimethylene)-bis[hexahydro-3,5-dinitro-triazine]. CA’s name for compd described in Vol 2, B159-L as Bis(1,3,5-triaz-3,5-dinitro-cyclohexylmethyl)-ether

Oxydine. A safety mining expl, patented by Turpin in 1888 in Fr. It was a mixt of equal parts of Dynamit No 1 (NG 75, kieselguhr 25%) and Zn oxide or sulfide.


Oxygen Balance. Oxygen balance (OB) is a measure of the fuel/oxygen ratio in a compound or mixt. In a qualitative sense OB has been successfully used in providing guidance to several practical as well as theoretical expl problems. Unfortunately OB has also been misused in attempts to obtain quantitative information which it is incapable of providing. Thus the main objective of this article is to point out what type of valid data OB can provide, and to critique published claims ascribing greater utility to OB than this simple concept permits.

Basically OB is an index of the deficiency or excess of oxygen, in the compound or mixt, required to convert all the carbon to CO$_2$ and all the hydrogen to H$_2$O. For an expl of the generalized molecular formula of $C_nH_{2n-N}O_{d}$

$$\text{OB to CO}_2 (\%) = \left[ \frac{d - 2a - 0.5b}{\text{formula weight}} \right] \times 1600 \quad (1)$$

Occasionally OB to CO is reported in the literature. In this case all the carbon is taken to form CO and all the hydrogen to form H$_2$O. Consequently

$$\text{OB to CO (\%) = } \left[ \frac{d - a - 0.5b}{\text{formula weight}} \right] \times 1600 \quad (2)$$

If the expl contains halogen atoms (X), eg $C_nH_{2n-N}O_{d}X_e$, and it is assumed that HX is formed in preference to H$_2$O, then
OB to CO₂ (%) = \left( \frac{d - 2a - 0.5(b - e)}{\text{formula weight}} \right) \times 1600 (3)

One would certainly think that the above assumption concerning HX is valid if X = F, or even if X = Cl. However, published values of OB for halogen-containing expls (Refs 1 & 10) have been calculated via Eq 1, i.e., the halogen is ignored.

If the expl contains metal atoms it is generally agreed that the stable metal oxide is first formed in preference to H₂O and CO₂. OB is then calculated via Eq 1 corrected for the oxygen required to form the metal oxide.

For complex expl mixts such as Dynamites it is convenient to compute OB for the individual ingredients and then calculate the OB for the mixt by algebraic addition. This method is also useful for aluminized expl mixts.

In what follows OB will always refer to oxygen balance to CO₂ unless otherwise stated. For convenience the % sign will not be used although it is to be understood that all subsequent OB’s are in percent.

The following illustrative examples will clarify the computation of OB:

1) **OB of TNT** (C₇H₅N₃O₆)
   From Eq 1 \( OB = \left( \frac{6 - (2x7) - (0.5x5)}{1600/227} \right) = -74.0 \)

2) **OB of NG** (C₃H₆N₂O₂)
   \( OB = \left( \frac{9 - (2x3) - (0.5x5)}{1600/227} \right) = +3.5 \)

3) **80/20 Tritonal** (TNT/Al)
   \( OB = \left( \frac{1.5 \times 1600}{27} \right) = -89, \)

and for TNT OB = -74
then OB (Tritonal) = 0.20(-89) + 0.80(-74) = -77.0

4) **Mercuric Fulminate** (Hg₂C₂N₂O₂)
   One oxygen atom is required to form HgO, therefore \( OB = \left( \frac{1 - 2 \times 2}{1600/285} \right) = -16.8 \)

Table 1 lists OB for common expls and expl ingredients. Note that most expls have negative OB’s.

Let us now examine the type of information that OB is capable of providing:

1) **Explosion fumes**. In a qualitative sense, OB can be used to predict the fumes generated by an expl. If the OB is positive, the fumes will contain highly toxic oxides of nitrogen. For negative OB, oxides of nitrogen will be minimal but the fumes may contain a substantial amount of CO. As discussed below, relatively little CO is produced under detonation conditions by high density expls.

   **Table 1**
   
<table>
<thead>
<tr>
<th>Substance</th>
<th>OB (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>+20.0</td>
</tr>
<tr>
<td>NH₄ClO₄</td>
<td>+34.0 (a)</td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>+27.0 (b)</td>
</tr>
<tr>
<td>EGDN</td>
<td>0.0</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>+47.0</td>
</tr>
<tr>
<td>NG</td>
<td>+ 3.5</td>
</tr>
<tr>
<td>TNM</td>
<td>+49.0</td>
</tr>
<tr>
<td>Al</td>
<td>-89.0</td>
</tr>
<tr>
<td>Cellulose (C₆H₉O₅)</td>
<td>-118.5</td>
</tr>
<tr>
<td>or Woodmeal</td>
<td></td>
</tr>
<tr>
<td>Charcoal</td>
<td>-266.7</td>
</tr>
<tr>
<td>Comp B</td>
<td>-43</td>
</tr>
<tr>
<td>DEGDN</td>
<td>-40.8</td>
</tr>
<tr>
<td>DNT</td>
<td>-114.4</td>
</tr>
<tr>
<td>HMX</td>
<td>-21.6</td>
</tr>
<tr>
<td>NC (12% N)</td>
<td>-38.7</td>
</tr>
<tr>
<td>NC (13.5% N)</td>
<td>-29</td>
</tr>
<tr>
<td>NGu</td>
<td>-30.8</td>
</tr>
<tr>
<td>NM</td>
<td>-39.0</td>
</tr>
<tr>
<td>PETN</td>
<td>-10.0</td>
</tr>
<tr>
<td>Pentolite</td>
<td>-42.0</td>
</tr>
<tr>
<td>RDX</td>
<td>-21.6</td>
</tr>
<tr>
<td>S</td>
<td>-100.0</td>
</tr>
<tr>
<td>Tetryl</td>
<td>-47.0</td>
</tr>
<tr>
<td>TNETB</td>
<td>-4.2</td>
</tr>
<tr>
<td>TNT</td>
<td>-21.6</td>
</tr>
</tbody>
</table>

(a) According to Eq 3
(b) According to Eq 1

However, upon expansion of the detonation products, substantial amounts of CO are formed if the expl OB is negative. This is illustrated in Table 2 by using data from Ref 11.

Comparison of the calculated and measured CO concns suggests that considerable expansion takes place even in the highly confined calorimeter samples of these measurements.

For many years OB has been used to classify Dynamites into various fume categories (Ref 2). This has been extended recently (Ref 8a) to AN-fuel explosives. It is customary to consider the Dynamite wrapper as part of the expl compn in computing OB, even though it is by no means certain to what extent the wrapper takes part in...
CO Production During Detonation and Upon Expansion

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Density (g/cc)</th>
<th>OB (%)</th>
<th>Detonation* CO moles/mole HE</th>
<th>Frozen Equilibrium at 1600°K &amp; 1 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN</td>
<td>1.74</td>
<td>-10</td>
<td>1.60 (0.13)</td>
<td>1.50</td>
</tr>
<tr>
<td>HMX</td>
<td>1.80</td>
<td>-21.6</td>
<td>1.06 (~0.06)</td>
<td>2.54</td>
</tr>
<tr>
<td>TNT</td>
<td>1.53</td>
<td>-74</td>
<td>1.98 (0.28)</td>
<td>5.86</td>
</tr>
<tr>
<td>NM</td>
<td>1.13</td>
<td>-39.4</td>
<td>0.55 (0.19)</td>
<td>0.75</td>
</tr>
</tbody>
</table>

*Measured by Ornellas (Ref 9) for confined samples; bracketed terms are computed by Mader (Ref 7) and interpolated to the density shown.

the detonation

2) Detonation Product Computation: Effect of Density

Current views (Refs 7 & 11) of detonation product equilibria in high density oxygen-deficient expls are that the available oxygen goes primarily into forming H₂O and CO₂, and any remaining oxidized carbon atoms form solid C. These equilibria are highly pressure-sensitive and as packing density decreases (which proportionately reduces the detonation pressure), increasing amounts of CO are produced. However, if the OB is positive or slightly negative, the amount of CO will vary only mildly with change in packing density. Thus OB provides qualitative information on the variation of CO production with HE packing density.

3) Explosive “Power”

At best, expl power is a somewhat nebulous quantity. If we consider relative power as measured in a Ballistic Mortar or Trauzl Block, then OB correlates reasonably well with relative power, provided these comparisons are made for similar expls. This is illustrated in Fig 1, where Ballistic Mortar measurements are respectively correlated with OB for nitro, nitramine, nitrate ester and aluminized expls. In general Ballistic Mortar measurements are more reproducible than Trauzl Block data. Consequently we have shown these in preference to Trauzl Block measurements. Correlation between Trauzl block data and OB are reported in Refs 1 & 8.

In the past, there have been a number of attempts to ascribe quantitative significance to correlations of OB with various detonation parameters (Refs 1, 3, 5, 6 & 8). In recent years these vain attempts appear to have subsided (see note at end of Refs).

Lothrop & Handrick (Ref 1) claimed to have correlated OB with “Power and Brisance”, with detonation velocity, and with heat of expls.

Martin & Yallop (Ref 3) have proposed a “corrected” OB and claim quantitative correlation (to within 2%!) of their corrected OB with detonation velocity.

Glowiak (Ref 5) claims that detonation velocity, heat of combustion and Trauzl Block test all correlate with a “true” OB for 25 nitro compounds (some containing diazo or azido groups). This writer has not seen his original publication & CA does not specify intelligibly what is meant by “true” OB.

Pagowski (Ref 6) proposes an “effective” OB (again undefined in CA) and claims a linear correlation of “effective” OB and detonation velocity.

Mustafa & Zahranc (Ref 8) prepared a series of substituted Tetryn, Penta, Hexyls & Nonyls. For each series they claim a correlation between the Martin & Yallop “corrected” OB, and impact or friction sensitivity, and Trauzl Block “power”. Their impact and friction sensitivity data appear to be monotonic functions of corrected OB, but the relation between corrected OB and Trauzl Block data appears to be complex.

Price (Ref 4) has shown convincingly that OB (garden variety, “corrected”, “effective”, or “true”) cannot per se determine the heat of expls or detonation. Using modern values of the heat of detonation, Q, this writer has convinced himself that there is not even fortuitous correlation between OB and Q.

Price also showed that detonation velocity, D, cannot be a linear function of OB, and even less
<table>
<thead>
<tr>
<th>Explosive</th>
<th>Density (g/cc)</th>
<th>Corrected OB*</th>
<th>Detonation Velocity (m/sec)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX</td>
<td>1.90</td>
<td>-14.3</td>
<td>9100</td>
<td>9162</td>
</tr>
<tr>
<td>RDX</td>
<td>1.80</td>
<td>-14.3</td>
<td>8750</td>
<td>8799</td>
</tr>
<tr>
<td>RDX</td>
<td>1.00</td>
<td>-14.3</td>
<td>5980</td>
<td>5929</td>
</tr>
<tr>
<td>TNT</td>
<td>1.64</td>
<td>50.0</td>
<td>6950</td>
<td>7001</td>
</tr>
<tr>
<td>Tetryl</td>
<td>1.71</td>
<td>-34.0</td>
<td>7850</td>
<td>7790</td>
</tr>
<tr>
<td>HNS</td>
<td>1.70</td>
<td>-50.0</td>
<td>7000</td>
<td>7210</td>
</tr>
<tr>
<td>NGu</td>
<td>1.55</td>
<td>-18.2</td>
<td>7650</td>
<td>7680</td>
</tr>
<tr>
<td>NM</td>
<td>1.13</td>
<td>-21.4</td>
<td>6300</td>
<td>6195</td>
</tr>
<tr>
<td>DATB</td>
<td>1.65</td>
<td>-38.6</td>
<td>7500</td>
<td>7430</td>
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<tr>
<td>BTF (C₈N₆O₆)</td>
<td>1.859</td>
<td>-33.3</td>
<td>8485</td>
<td>8320</td>
</tr>
<tr>
<td>PETN</td>
<td>1.70</td>
<td>-12.25 (a)</td>
<td>8300</td>
<td>8525</td>
</tr>
<tr>
<td>DEGDN</td>
<td>1.38</td>
<td>-42.8 (a)</td>
<td>6760</td>
<td>6400</td>
</tr>
<tr>
<td>DDNP</td>
<td>1.60</td>
<td>-58.8 (a)</td>
<td>6900</td>
<td>6570</td>
</tr>
<tr>
<td>NC (13.45% N)</td>
<td>1.20</td>
<td>-33.3 (a)</td>
<td>7300</td>
<td>6110</td>
</tr>
<tr>
<td>TNETB</td>
<td>1.76</td>
<td>-15.0 (a)</td>
<td>8290</td>
<td>8623</td>
</tr>
<tr>
<td>LX-04</td>
<td>1.86</td>
<td>-19.8</td>
<td>8460</td>
<td>8830</td>
</tr>
<tr>
<td>Comp B</td>
<td>1.72</td>
<td>-28.1</td>
<td>7990</td>
<td>8110</td>
</tr>
<tr>
<td>Pentolite</td>
<td>1.66</td>
<td>-33.3</td>
<td>7465</td>
<td>7650</td>
</tr>
<tr>
<td>EGDN</td>
<td>1.48</td>
<td>0</td>
<td>7300</td>
<td>8110</td>
</tr>
<tr>
<td>EGDN</td>
<td>1.48</td>
<td>-14.3 (b)</td>
<td>7300</td>
<td>7650</td>
</tr>
<tr>
<td>BTNEU</td>
<td>1.60</td>
<td>0</td>
<td>8100</td>
<td>8370</td>
</tr>
<tr>
<td>BTNEU</td>
<td>1.60</td>
<td>-6.2 (b)</td>
<td>8100</td>
<td>8360</td>
</tr>
<tr>
<td>1 mole NM/</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 moles TNM</td>
<td>1.40</td>
<td>0</td>
<td>6780</td>
<td>7810</td>
</tr>
<tr>
<td>NG</td>
<td>1.59</td>
<td>+17.5 (a)</td>
<td>7580</td>
<td>9108</td>
</tr>
<tr>
<td>Nitromannite</td>
<td>1.73</td>
<td>+21.05 (a)</td>
<td>8260</td>
<td>9810</td>
</tr>
<tr>
<td>TNM</td>
<td>1.64</td>
<td>+46.1</td>
<td>6360</td>
<td>10290</td>
</tr>
</tbody>
</table>

*Corrected OB = \( \Omega = (d-2a-0.56)100/n + 100w/n \)

where \( n \) = number of atoms in the molecule

\( w \) = summation of O atoms according to their linkages, thus

\( w = 0 \) for nitro or nitramine oxygens

\( w = 1 \) for nitrate (\(-\text{O}--\text{N}--) \) oxygens

\( w = 1.8 \) for carboxyl oxygens

\( w = 2.0 \) for alcohol oxygens

\( \pm \) take + if first term is +

\( \pm \) take - if first term is -

Other symbols as defined for Eq 1

**\( D_{\text{calc}} = 2509 + 3793\rho + 13.25\Omega + 12.81\rho\Omega \)**

where \( \rho \) = packing density of expl

(a) \( w \) term included in \( \Omega \) computation

(b) \( w \) term included in \( \Omega \) computation but negative sign is used for \( \pm \)**
likely a linear function of OB and packing density

However, as shown in Table 3 (assembled by
this writer from data in Refs 7, 10 & 12 and the
Martin & Yallop equation), computed and mea-
sured D's agree surprisingly well for a variety of
explos having negative "corrected" OB, although
agreement is not within the 2% claimed by Martin
& Yallop. However, correlation between "corrected"
OB and D breaks down completely (as shown in
Table 3) for explos with positive OB. Also, the
correlation for the nitrate esters (second grouping
from top of Table 3), is not as good as for the
other oxygen-deficient explosives.

To sum up, OB is a concept that can provide
useful qualitative information. It should not be
used for quantitative correlations except (and then
only judiciously) for correlation between chemi-
sically similar explosives.

Written by J. ROTH

PolonSciShim 10, 475 (1963) & CA 58, 7780 (1963) 7) C.L. Mader, LA 2900 (1963)
8) A. Mustafa & A.H. Zahran, JChemEngData 8, 135 (1963) & CA 58, 5444 (1963) 8a) H.

Note: CA was searched from 1964-1975 but no refs to OB were found

Oxyliquid. There is some confusion regarding this
term; it is sometimes applied to liquid air explo-
substances and sometimes to liquid oxygen explosives.
However, there is no doubt that it was applied to
liquid air explosives prior to the appearance of
commercial liquid oxygen.

According to Marshall (Ref 2), "Oxyliquid"
refers to an expl invented by Linde in 1895 (Ref
1) which consisted of liquid oxygen absorbed in
wadding, charcoal, or other organic material.

Barnett (Ref 3) calls "Oxyliquid" the "liquid
air explosive".

Davis (Ref 4) states, "Liquid oxygen explo-
substances were invented in 1895 by Linde, who de-
veloped a successful machine for the liquification
of gases. The 'Oxyliquids', as he called them, pre-
pared by impregnating cartridges of porous com-
bustible material with liquid oxygen or liquid
air . . . .". Also according to Davis, "Liquid oxygen
explosubstances were at first made from liquid air, more
or less self-enriched by standing; the nitrogen (bp
-195°) evaporating faster than the oxygen (bp
-183°) but it was later shown that much better
results followed from the use of pure liquid oxygen"

Cooke (Ref 5) defines "Oxyliquid" as a blasting
explosion formed by rapidly mixing liquid air, rich in
oxygen, with powdered charcoal, petroleum residues,
or cotton wool.

In conclusion, it may be said that, if the original
term "Oxyliquid" was applied to "liquid air explo-
substances", it might be well to leave it so, especially as
"Liquid Oxygen Explosives" have been given the

Oxygen Fluoride (Oxygen Difluoride, Fluorine
Monoxide). OF₂, mw 54.00; colorl, unstable gas;
mp -224°, bp -145°, sl sol in w and alc. It has
been suggested as an oxidizer for rocket proplnts
(Ref 1)
convenient acronym “LOX”
Also see under Liquid Air and Liquid Oxygen Explosives in Vol 7, L19-R to L26-L

\( \text{N}_{1}\text{-or N} \text{-Oxytetrazole (1-Oxy-isoTetrazole, Iso-oxotetrazole). } \text{CH}_2\text{N}_2\text{O}_4 \text{, mw 86.01, N 65.11%,} \)

\[ \text{HC:N(O):NH} \]

\[ \text{N——N} \]

\( \text{ethyl acetate, mp 155°, bp starts to decomp at about 160°. Easily sol in w, methanol and alc; diff sol in eth, insol in benz} \)

It was first prepd by Palazzo by the interaction of hydrazoic acid and fulminic acid at low temp. Can also be prepd by acidifying Na oxy-iso-tetrazole with dil sulfuric acid (Refs 1, 2 & 4)

\( \text{It explds on strong impact, and forms salts, some of which are expl} \)

**Sodium salt.** \( \text{NaCHON}_4\text{H}_2\text{O} \). According to Rosati (Ref 3), this salt occurs in two cryst forms; 1) as pale-yellow cryst and 2) as colorl tablets; both belonging to the pinacoidal class of the triclinic system; mp, loses its water at 120–130° and explds at 240°. Easily sol in w, diff sol in aq alc, insol in abs alc and other org solvents

It was first prepd by Palazzo as a by-product in the prepn of 1-hydroxytetrazole from hydrazoic acid (2 mols) and Na fulminate (1 mol) (Refs 1, 2 & 4). The Na salt may serve for the prepn of free iso-oxotetrazole, as well as its salts, such as:

**Mercury salt.** White solid, expl. Can be prepd by treating the Na compd with a sol Hg salt

**Silver salt.** White solid, expl. Can be prepd by treating the Na compd with a Ag salt


**Ozon.** \( \text{O}_3 \), mw 48.00, triatomic oxygen, the most reactive form of oxygen; a bluish, expl gas or blue liq. It is found in the atm in varying proportions (about 0.05ppm at sea level), since it is produced continuously in the outer layers of the atm by the action of solar UV radiation on the oxygen of the air. In the laboratory ozone is prepd by passing dry air between two plate electrodes connected to an alternating current source of several thousand volts. Machines for the production of ozone,
known as ozonizers, are marketed commercially. More generally, ozone is formed whenever oxygen is subjected to intense photochemical or electrical radiation (Ref 5).

At ordinary temps ozone is a blue gas, but at the concns at which it is normally produced the color is not noticeable unless the gas is viewed thru considerable depth. At $-112^\circ$C, ozone condenses to a dark-blue liq which is easily expid, as are concd ozone-oxygen mixts (above about 20% ozone), in either the liq or the vapor state. Explan may be initiated by minute amounts of catalysts or organic matter, shocks, electric sparks, sudden changes in temp or pressure, etc (Ref 4). Other properties of ozone are given in Table 1.

Table 1
Properties of Pure Ozone ($O_3$) (From Ref 4)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point, °C</td>
<td>$-192.5 \pm 0.4$</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>$-111.9 \pm 0.3$</td>
</tr>
<tr>
<td>Critical temperature, °C</td>
<td>$-12.1$</td>
</tr>
<tr>
<td>Critical pressure, atm</td>
<td>54.6</td>
</tr>
<tr>
<td>Critical volume, cm$^3$/mole</td>
<td>111</td>
</tr>
</tbody>
</table>

Density and vapor pressure of liquid

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Density, g/cm$^3$</th>
<th>Vapor pressure, torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-183$</td>
<td>1.574</td>
<td>0.11</td>
</tr>
<tr>
<td>$-180$</td>
<td>1.566</td>
<td>0.21</td>
</tr>
<tr>
<td>$-170$</td>
<td>1.535</td>
<td>1.41</td>
</tr>
<tr>
<td>$-160$</td>
<td>1.504</td>
<td>6.73</td>
</tr>
<tr>
<td>$-150$</td>
<td>1.473</td>
<td>24.8</td>
</tr>
<tr>
<td>$-140$</td>
<td>1.442</td>
<td>74.2</td>
</tr>
<tr>
<td>$-130$</td>
<td>1.410</td>
<td>190</td>
</tr>
<tr>
<td>$-120$</td>
<td>1.378</td>
<td>427</td>
</tr>
<tr>
<td>$-110$</td>
<td>1.347</td>
<td>865</td>
</tr>
<tr>
<td>$-100$</td>
<td>1.316</td>
<td>1605</td>
</tr>
</tbody>
</table>

Density of solid ozone, g/cm$^3$, at 77.4 K: 1.728
Viscosity of liquid, cP, at 77.6 K: 4.17
at 90.2 K: 1.56
Surface tension, dyn-cm, at 77.2 K: 43.8
at 90.2 K: 38.4
Parachor at 90.2 K: 75.7
Dielectric constant, liquid, at 90.2 K: 4.79
Dipole moment, debye: 0.55
Magnetic susceptibility, cgs units, gas: 0.002 x 10$^{-6}$
liquid: 0.150
Heat capacity of liquid from 90 to 150 K: $C_p = 0.425 + 0.0014(T-90)$
Heat of vaporization, kcal/mole, at $-111.9$ °C: 3410
at $-183$ °C: 3650

Heat and free energy of formation

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta H_f$, kcal/mole</th>
<th>$\Delta G_f$, kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas at 298.15 K</td>
<td>34.15</td>
<td>38.89</td>
</tr>
<tr>
<td>liquid at 90.15 K</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>hypothetical gas at 0 K</td>
<td>34.74</td>
<td></td>
</tr>
</tbody>
</table>
Liq ozone is miscible in all proportions with CClF₃, CCl₂F₂, CH₄, CO, F₂, NF₃ and OF₂ liquids, and forms two-layer systems with A, CF₄, N₂ and O liquids. The limited miscibility of ozone in oxygen is of practical importance because the dense, ozone-rich layer which settles to the bottom, is easily expld. The mutual solubility of the two liqs decreases when the temp is reduced. Thus, liq ozone and oxygen are completely miscible above 93.2°K (at which temp the total pressure is 1.25 atm), but at 90.2°K (the atm-bp of liq oxygen), there is separation into two layers, containing 17.6 and 67.2 mole % ozone, respectively. At still lower temps, the separation becomes even more pronounced (Ref 4).

Uses. In terms of ordnance application, during WWII, German scientists worked overtime on an ozone-propelled rocket designed to bombard New York City from European launching platforms. However, they were unable to handle the material without spontaneous detonation (Ref 1). Later investigations into the possibility of using liq ozone or, strictly speaking, mixts of liq oxygen with liq ozone, were carried out by the Armour Research Foundation. According to Platz & Hersh (Ref 2), liq ozone or a mixt of liq ozone and oxygen may be obtained by introducing oxygen, carefully purified from organic impurities, into an ozonizer, where the mix is irradiated and the ozone liquified (−111.9° under atm press); the oxygen escapes thru an exit pipe. If a mixt of liq ozone with oxygen is to be obtained, the gases discharged from the ozonizer are introduced into the liq oxygen after being cooled.

A.G. Streng (Ref 3), in an excellent review article on the combustion and explosive properties of ozone, states, “In recent years ozone has attracted attention as a high energy chemical with a potential use in powerful propellant and explosive systems. Being an endothermic compd and a highly active oxidizer, ozone can burn and detonate by itself and in combination with various fuels. Ozone alone represents the simplest combustible and explosive system. It has often been used as a model in the theoretical interpretation of detonation and combustion phenomena, but inability to handle highly concentrated ozone in the past has prevented its experimental investigation for a long time. When combined with fuels, ozone produces systems with much higher energy content than does oxygen.” Streng covers flammability or explosibility limits, burning and detonation velocities, and dangerous characteristics of gaseous, liq and solid ozone, both alone and in admixture with fuels.

Toxicity and Hazards. The odor of ozone can be detected in concns as low as several parts per hundred million by vol (pphm). The threshold limit value (TLV) is 0.1 ppm or 0.2 mg/m³; its toxic dose level (TDL), 50% kill concn is 2 ppm (Ref 6).

Pure 100% liq ozone may be kept safely at 90°K (cooled by liq oxygen) for indefinite periods of time, but the smallest provocation, such as a spark or fast warming, even only up to bp (161°K), causes detonation. The evapn of liq ozone, for example, in the process of the prepn of pure gaseous ozone is, therefore, a dangerous procedure (Ref 3, p 224).

Liq ozone in concns greater than 30% by wt is extremely unstable, and may expld on contact with even minute traces of organic matter. Not only all precautions for handling liq oxygen, but also extra precautions for a sensitive expl must be observed (Ref 4, p 430).

Solid ozone is very expld, and at its freezing pt is very sensitive. If liq ozone in a tube is suddenly immersed to the full length of the ozone layer into solid nitrogen, detonation usually occurs. This probably is due to the fact that ozone crystals appear over the entire height of the tube, and by friction of one set of crystals against another, enough heat is developed to initiate ozone detonation. On the other hand, if only the bottom of the ozone tube is inserted into solid nitrogen, the crystallization of solid ozone proceeds slowly from the bottom toward the top and no detonation takes place (Ref 3, p 225).

Hazardous reactions reported in the literature between ozone and anilne, benz, bromine, diallyl methyl carbrol and acetic acid, diethyl ether, dinitrogen pentoxide, ethylene, hydrogen bromide, hydrogen iodide, nitric oxide, nitrogen dioxode, nitrogen trichloride, nitrogen trisiodide, NG, organic liquids, organic matter, and stilbene are detailed with pertinent refs in Ref 7.

Ozone Explosives or Ozonides

The principal organic reaction of ozone is its addition to the carbon-carbon double bond of an ethylenic compound. The resulting ozone-olefin addition compound is known as an ozonide. Decomposition of the ozonide gives a mixture of oxygenated products containing carbonyl compounds and acids. Ozone also adds to the carbon-carbon triple bond of acetylenic compounds, the usual products being diketones and carboxylic acids. In polynuclear aromatic compounds, the various carbon bonds and atoms have different reactivities. The reaction with ozone is more complex and the composition of products is difficult to predict.

The reaction of ozone with an unsaturated organic compound was reported more than a century ago (Schönbein, *J. Prakt. Chem.* 66, 282 (1855)), however, complete explanation of this reaction has not been made until recent times. In 1905, Harries (Ref 1) postulated that the addition of ozone to an olefin resulted in the formation of an ozonide according to the formula:

\[
\text{R} \quad \text{C} = \text{C} \quad \text{R} + \text{O}_3 \rightarrow \text{R} \quad \text{C} = \text{C} \quad \text{R} \quad \text{O} = \text{O} = \text{O} 
\]

A compound of this structure should on reduction, give a glycol. However, many attempts by various investigators failed to give the expected reduction product.

About twenty years later, Staudinger (Ref 2) suggested that ozonides had the following structure:

\[
\text{R} \quad \text{O} \quad \text{C} \quad \text{R} 
\]

He called this compound (1) an *isozonide*. Since the carbon-carbon bond was broken, glycols would not be formed, and the decomposition products would be those which had already been observed. As the primary ozone-olefin addition product, Staudinger postulated a *molozone* to which he ascribed formula (2),

\[
\begin{align*}
\text{R} & \quad \text{C} = \text{C} \quad \text{R} \\
\text{R} & \quad \text{O} = \text{O} = \text{O} \quad \text{R}
\end{align*}
\]

The molozone was unstable and would either rearrange into the isozonide or form polymers. While Staudinger's theory explained the formation of the major products, some of the by-products could not be accounted for. The greatest step toward complete elucidation of the ozonolysis reaction was made by Cregee (Ref 3) in the 1950s. From a study of ozonolysis in various solvents and the constitution of the products, Cregee proposed these reactions:

\[
\begin{align*}
\text{R}_1 & \quad \text{C} = \text{C} \quad \text{R}_3 \quad \text{O}_3 \quad \text{R}_2 & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{R}_4 \quad \rightarrow \\
\text{R}_1 & \quad \text{R}_3 \quad \text{R}_2 \quad \text{R}_4 \quad \text{C}(+) \quad \text{O} \quad \text{O}(+) \quad \text{C} \quad \text{O} \quad \text{O}(+) \quad \text{R}_3 \quad \text{R}_2
\end{align*}
\]

The primary ozone-olefin addition product splits into a molozone zwiterion (3). The zwiterion (3) then stabilizes by splitting into a carbonyl compound (4) and another zwiterion (5). The observed ozonolysis reaction products could now be explained by the reaction of the zwiterion (5) with itself and other reactive compounds present in the reaction mixture (Ref 4).

Because ozonides are active oxygen compounds, they can be used as oxidizing agents, polymerization catalysts, bleaching agents, and germicides. But their instability makes it difficult to prepare them in good yields and to use them safely in reactions. Ozonides or ozonolysis products of the olefin and zwitterion (5) must be cooled to maintain the desired temp (Ref 4).

Following below are some examples of ozonides, reported primarily in the older literature:

*Refs.*: 1) C.D. Harries, Ann 343, 311 (1905); Ibid 374, 288 (1910); "Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen", J. Pranger, Berlin (1916) 2) H. Staudinger, Ber 58, 1088 (1924) 3) R. Cregee,

Acetyleneozoneide. C₂H₂O₃, has never been isolated. According to Briner et al (Ref 3), ozonization of acetylene in gaseous form resulted in expls. However, when the ozonization was conducted in an anhyd solvent by one of the methods described by Harries (Ref 2) for ozonization of unsaturated hydrocarbons, Briner was able to obtain some crystals which were unstable and exploded before they could be examined. When the solvent used in the prepn was rapidly evaporated, the residue exploded
Refs: 1) Bell, not found  2) C.D. Harries, Ann 374, 288 (1910)  3) E. Briner & R. Wunenburger, Helv 12, 786 (1929) & CA 23, 5156 (1929)

Allyacetone-oxo-ozonide (Hexen-(1)-on-(5)) ozonide in Ger). C₅H₁₀O₅, syrup, d 1.1814g/cc. Can be prep'd by treating allylacetone with ozone. It is very expl
Refs: 1) Bell, 734  2) C.D. Harries & K. Langheld, Ann 343, 348 (1905)

Amyleneozoneide (Trimethylenezyleneozoneide). Harries et al (Ref 2) claimed to have prep'd two expl products on treating trimethylene (C₃H₁₀) with ozone. The first corresponded to the formula C₅H₁₀O₃, while the second, more expl than the first, C₂H₁₀O₄ (amylene-oxo-ozonide). Both substances were syrups of different densities and refractive indices (values not given)
Refs: 1) Bell, not found  2) C.D. Harries & K. Haeffner, Ber 41, 3099 (1908)

Benzene Triazoneide (Oxobenzene, Benzolithiazonide in Ger). C₆H₆O₉ (probable structure given by Beilstein, Ref 1); white, amorph, si volatile solid; sol in benz, insol in alc, eth, chl, CS₂ and ligroin. Prep'd by Renard (Ref 2) and Harries et al (Refs 3 & 4) by passing ozone thru pure benz (thiophene free), cooled to 5–10°
It is an extremely expl compd. It detonates violently on impact, heat or when brought into contact with warm water, concd sulfuric acid or concd H₂O₃. When treated with ice water, it is transformed into a crystalline material which explodes at the slightest touch
According to A. Pérez Ara (Ref 6), it detonates when heated to as low as 50°, and Stettbacher (Ref 5) states that 1 kg develops about 2,000kg cal on expl

Biphenyl (or Diphenyl) Tetraozonide. C₁₂H₁₀(O₃)₄. It was first prep'd in 1905 by Harries (Ref 1), and again in the USA during WWII, where it was found to be too unstable and too sensitive for military or commercial use as an expl
Ref: 1) C.D. Harries, Ann 343, 337 (1905)

n-Butadieneoazoucoubuc Oxonide (n-Butadienuerubber Oxonide, Normaler Butadienkautschuk in Ger). (C₄H₆O₃)₉(7). Was prep'd by the ozonization of a polymer called "Normaler Butadienkautschuk" in Beilstein (Ref 1), dissolved either in chl or CCL₄. The caoutchouc was prep'd by Harries (Ref 2) by heating butadiene-1,3 (also called divinyl or endthene) in a sealed tube for 10 days at 110–120° with acetic acid
When chl was used as solvent in the ozonization, the resulting ozonide was an expl oil. When CCl₄ was used as solvent, the resulting product was a non-expl solid
Several other ozonides were prep'd from butadiene polymers, but it was not stated whether or not they were expl
Refs: 1) Bell 1, (109)  2) C.D. Harries, Ann 383, 206 (1911)

Butylene-oxo-ozonide Dimer (Dimeres Butylene-ozonide in Ger). (C₄H₆O₃)₂, oil, mp –80°, d 1.1604g/cc at 19/19°, RI 1.43167 at 19°. Was obtained together with other products on treating β-butylen, CH₃CH=CHCH₃, dissolved in methyl
chloride, with 14% ozone. Easily sol in petr eth and w. When carefully heated, it goes to monomeric butylenezonide (see below), but explos very violently when heated to about 125°C (Ref 2). The same investigators prep butylene-oxo-zenide monomer, to which they assigned the formula CH₃.CH.CH₂.CH₃.

This oily material was not examined for expl properties
Refs: 1) Beil 1, (85) 2) C.D. Harries & F. Evers, Ann 390, 245—247 (1912)

β-Butylenezonides (Buten-(2)-azonid, Pseudobutyle-azonid, or α-α-Dimethyl-ethylene-azonid in Ger). The following compds were prep by Harries et al (Refs 1 & 2):

Butylene Ozone Monomer (Monomers Normales Butylenezonid in Ger). C₄H₅O₃, very vol oil, bp 15—16°C at 20mm, d 1.0217g/cc at 22/22°C, RI 1.3855 at 22°C. Was prep by Harries and then by Briner et al (Ref 3) by ozonization of β-butylene. Briner prep it by dissolving β-butylene in methyl chloride, cooling the soln to —80°C, and passing ozonized air thru it
The compd is fairly stable at room temp and is only slowly decompd by cold w. It reacts with hot w (70—75°C), yielding CH₃COOH, HCOOH and CH₄. It is sol in org solvents; expls violently when heated under confinement to about 125°C; burns quickly when unconfined and touches with a flame or hot object

Butylene Ozone Dimer (Dimers Normales Butylenezonid in Ger). (C₄H₅O₃)₂, thick syrup, sol in org solvents. Was obtained, together with the monomer, by treating β-butylene with 8—10% ozone; could not be distilled. Explod on heating in a tube to about 125°C
Briner and Meier (Ref 3) prep ozonides of all three butlenes (α, β and iso) by ozonization in the dil gaseous phase, both in the presence and abse of w. The same compds were obtained by ozonization at low temps of butlenes, dissolved in non-aqueous solvents. The resulting ozonides, only sol sol in w, were very expl

Iso-Crotonicaicidozone (Isocrotonisäure-azonid in Ger). C₄H₅O₄, clear syrup, decompd by w or on standing; extremely expl. Was prepd by the action of ozone on a chloroformic soln of iso-crotonic acid, CH₃.CH.CH.COOC
Note: Crotonic acidozonide was prepd by Briner and Franck (Ref 3)

Cyclohexene-oxo-azonid Polymer (Polymeres Cyclohexen-oxo-azonid in Ger). (C₆H₁₀O₄)ₓ, amorph substance, mp 115—120°C decompn, insol in org solvents. Was prepd, together with polymeric cyclohexenezone (see below), by passing ozone thru a soln of cyclohexene in chf or CCl₄ (Ref 3). Although its expl properties were not examined, it might be presumed that, inasmuch as the polymeric ozone (C₆H₁₀O₃)ₓ is a strong expl (see below), the compd (C₆H₁₀O₄)ₓ, with with one additional oxygen per each six carbons, should be even a stronger expl

Cyclohexene-oxo-azonid Dimer (Dimers Cyclohexen-oxo-azonid in Ger). (C₆H₁₀O₄)₂, solid, mp 115—120°C. Obtained in small quantities by passing strong ozone thru a chf soln of cyclohexene. Its expl properties were not examined

Cyclohexene Ozonides:
Monomeric Cyclohexenezone. C₆H₁₀O₃, bp 59—60°C at 12mm, diffcultly sol in cold w, easier in hot w (with decomp). Was prepd by Harries & Seitz (Ref 2), together with polymeric forms, by treating cyclohexene dissolved in hexane with ozone
Polymeric Cyclohexenezone. (C₆H₁₀O₃)ₓ, solid compd, mp 60—65°C; sol in boiling alc, insol in eth & chf; explds violently on heating to 140—150°C. Can be prepd, together with the monomer (see above) and the polymer (see below) by passing ozone thru cyclohexene dissolved in cooled hexane, chf or CCl₄
Polymeric Cyclohexenezone. (C₆H₁₀O₄)ₓ, amorph substance, mp 115—120°C (with decomp), insol in org solvents, explds on heating. Can be
prepd, together with the two ozonides above, by passing ozone thru cyclohexene dissolved in cooled chl of CCl₄.

Some cyclohexene-oozozonides were prep'd and studied in the USA during WWII, but were found to be too unstable and insufficiently powerful to be used as expls (Ref 6).


Cyclopentane-ooxonides. A monomer, C₅H₄O₃, was prep’d (Ref 2) by the ozonization of cyclopentene dissolved in CCl₄. It is a yel, volatile liq with a penetrating odor; sol in chl, ethyl acetate and acetic acid; is decomp'd explosively by conc'd sulfuric acid; expls on heating.

The polymer, (C₅H₄O₃)ₓ, was prep’d (together with some monomer) on passing ozone thru a chloroformic soln of cyclopentene. It is a cryst compd, insol in org solvents; reacts violently with conc'd sulfuric acid; a powerful expl.


Cyclopentane Oxonides. The monomer, C₅H₆O₃, was prep’d by passing a small quantity of ozone thru cyclopentane dissolved in hexane cooled with an ice-salt mixt (Ref 2). A liq, bp 60–62° at 10mm, it sometimes expld on distillation.

The same investigators obtained the polymer, (C₅H₆O₃)ₓ, by treating ozone dissolved in ethyl chloride, with ozone. A cryst compd, insol in most org solvents, it expld at 94°.


Cyclopentadieneoxonide (Polydicyclopentadiene diozonide, Polycyclopentadieneoxonoid in Ger). (C₂H₄O₃)ₓ or (C₁₀H₁₂O₄)ₓ; amorph powd, mp 120–125° (starts to sinter at 114°). The polymeric ozonide is insol in common org solvents, dissolves in boiling AcOH with decomp’n, is decomp’d by boiling w.

It is very expl.

Was prep'd by Staedinger & Bruson (Ref 2) by saturating a CCl₄ soln of dicyclopentadiene, C₁₀H₁₂, with 5% ozone.

Refs: 1) Beil 1, 459, (238) & [391]; Ibid 5, [78]  2) H. Staedinger & H.A. Bruson, Ber 58, 1095 (1925)

Diallyldiozonide (1,5-Hexadienediozonide, Hexadien-1,5-diozonid in Ger). C₆H₁₀O₆, syrupy, expls strongly on heating. Was prep’d by Harries & Turk by treating a cooled chloroformic soln of diallyl, CH₂=CH-CH₂-CH₂=CH₂, with ozone (Ref 2).

Refs: 1) Beil 1, 254  2) C.D. Harries & H. Turk, Ann 343, 360 (1905)

Isodicyclopentadienediozonide (Isocyclopentadieonidozonide in Ger). C₁₀H₁₂O₅, white hygr powder, mp 95–98° (expls on heating above mp); decomp in humid air. It is easily sol in acet & pyridine, sol in acetic acid; sl sol in ethyl acetate, benz, CCl₄ and CS₂; insol in eth & petr eth.

Was prep’d by passing 5% ozone thru an ethyl acetate soln of dicyclopentadiene, C₁₀H₁₂ (Beil 5, 495, (238) & [391]), for 20 hours.

Refs: 1) Beil 5, [391]  2) H. Staedinger & H.A. Bruson, Ber 58, 1094 (1925)

Iso-dicyclopentadiene-ooxidozonide, C₁₀H₁₂O₇; white, hygr solid; mp 105–108° (expls on heating above mp); solubility similar to above compd.

Was prep’d by passing 5% ozone for 48 hrs thru dicyclopentadiene dissolved in ethyl acetate.

Refs: 1) Beil 5, [392]  2) H. Staedinger & H.A. Bruson, Ber 58, 1095 (1925)

2,5-Dimethylhexadiene-1,5-diozonide. C₆H₁₄O₆; thick yel syrup, decomp on standing, expls violently on heating. Prep’d from 2,5-dimethylhexadiene-1,5 and ozone.

Refs: 1) Beil 1, 259  2) C.D. Harries & H. Turk, Ann 343, 367 (1905)

Diphenyltetrazonide. C₁₂H₁₀O₁₂; colorl, very volatile crysts; expls violently on heating. Prep’d by treating a chloroformic soln of diphenyl with ozone.

Refs: 1) Beil 5, 579 & [482]  2) C.D. Harries
Ethylene Ozonide. C₂H₄O₃; colorless, unpleasant-smelling oil; mp, becomes lustrous at −80°, bp, 18° at 16 mm, 20° at 17 mm; d 1.265 g/cc at 17.5/17.5°. Was first prep by Harries & Koetschau (Ref 2) by passing ozonized (7%) air thru a soln of ethylene in methyl chloride, cooled to −70°.

Ethylene ozonide expls violently on heating, impact or friction, or when poured into concd caustic soln (Ref 3).


Ethylperoxide (Called Ethylperoxide by Berthelot). Berthelot obtained a fruity-smelling liq by passing ozone in an atm of CO₂, thru well-cooled (ice-salt mixt) absolute ether. After removing the ether by vac, the residue was distilled at 20 mm, and a fraction at 40–50° was collected. It was a colorless mass, which gave colorless crysts on strong cooling (Ref 1).

According to Berthelot, the formula of this compd is (C₂H₃)₂O₃, which requires C=58.54%, H = 12.19% and O = 29.27%. The substance expld during the last stages of the work.

Harries and Weiss (Ref 2) repeated Berthelot’s exp, but obtained a product of lower C and H content (C = 15.3 to 25.6%; H = 6.5 to 7.1%), and higher O content (O = 67.9 to 77.7%). The material expld when heated on a Pt foil.

Refs: 1) M. Berthelot, CR 92, 895 (1881) 2) C.D. Harries & V. Weiss, Ann 343, 375 (1905)

Iso-Eugenolozonide. C₁₀H₁₄O₅; yel oil from ethyl acetate & petr ether. Can be prep’d by passing 1% ozone thru isoeugenol dissolved in hexane. This gave a ppt of heavy syrup, which was a weak expl, insol in ethyl acetate, hexane or petr ether. After evapg the hexane at 20° and reduced pressure, a small quantity of highly expl yellow oil was obtained. It was not further examined.

Refs: 1) Beil 6, (470) 2) C.D. Harries & R. Haarman, Ber 48, 36 (1915)

Fumaric Acid Ozonide. C₄H₄O₅, a very expl compd, prep’d by treating a soln of fumaric acid in methanol, cooled to −60°, with ozone.

Ref: E. Briner & D. Franck, Helv 21, 1297–1313 (1938) & CA 33, 535 (1939)

α-Hexylene Ozonide (Hexen-(1)-ozonid in Ger). C₆H₄O₃; colorless oil, bp 60° at 12 mm, d 0.9709 g/cc at 18/18°, RI 1.4059 at 18°. This product was isolated by Harries et al from an oil having a compn between C₆H₄O₃ and C₆H₄O₂. The oil was prep’d by ozonization of a chloroethyl or hexanic soln of α-hexylene, CH₃(CH₂)₂.CH₂.CH₂

The ozonide C₆H₄O₂ was sol in common org solvents with the exception of petr ether, in which it was difficult sol; it was also difficult sol in w. It is an expl compd.

Another substance isolated from the crude oil was also an expl; bp ca 60° at 12 mm, d 0.9938 g/cc at 22.5/22.5°, RI 1.3947 at 22.5°. It probably was hexylene-oxo-ozonide, C₆H₄O₄.

Refs: 1) Beil 1, (90) 2) C.D. Harries & K. Haefliger, Ann 374, 331–35 (1910)

Isoprene Rubber Ozonides (Isoprenkautschuk-ozonid or Künstlicher Isoprenkautschuk Diozonid in Ger). (C₅H₈O₃), several products corresponding to this formula are known:

Normal-Isoprene Rubber Ozonide (Ozonid des Normaler Isoprenkautschuk in Ger). A very thick oil, sol in hot w, puffs off violently on heating. Prep’d by Harries et al by passing 12% ozone thru a chlf or CCl₄ soln of n-isoprene rubber for several hours.

α-Isoprene Rubber Ozonide (Ozonid des Natrium-isoprenkautschuk in Ger). A thick, colorless oil from ethyl acetate & petr ether. It is a more powerful expl than the above compd. Prep’d by passing 6–7% ozone thru a chloroformic soln of α-isoprene rubber.

D-Limonenediozone Polymer (Diozonid des d-Limonens in Ger). \( \text{C}_{10}	ext{H}_{18}	ext{O}_{6} \times 3 \), white, solid, mp 60–65°C, explods on heating to about 85°C. Sol in w, alc, eth, benz; v sol in chlf, ethyl acetate and AcOH. Prepbd by ozonization of d-limonene, \( \text{C}_{10}	ext{H}_{16} \), dissolved in chlf or CCl4

**Note:** Limonenediozone was first described by H. Neresheimer, Dissertation, Kiel (1907)

**Refs:** 1) Beil 5, (71) 2) C.D. Harries & H. Adam, Ber 49, 1035 (1916)

Mesityloxideozonide. \( \text{C}_{6}	ext{H}_{10}	ext{O}_{3} \), liq, d 1.0754 g/cc at 18.5/18.5°C, RI 1.3941, sol in most org solvents except petr ether. Prepbd by passing dil ozone (12–14% concn) and \( \text{CO}_2 \) thru well cooled mesityleneoxide. Decomps on heating, but is fairly stable at room temp

**Refs:** 1) Beil 1, (383) 2) C.D. Harries & H. Turk, Ber 38, 1631 (1905) 3) Ibid, Ann 374, 340 (1910)

Mesityloxideperozonide. \( \text{C}_{6}	ext{H}_{10}	ext{O}_{3} \), green syrup, highly expl, catches fire spontaneously on standing at room temp. Prepbd by saturating mesityloxide with ozone at very low temp

**Refs:** 1) Beil 1, 738 & 7, 953 2) C.D. Harries et al, Ber 36, 1933 (1903) 3) Ibid, 38, 1631 (1905)

Methyleugenolozonides. Mono- and triozonides are known:

**Monozozonide des Eugenolmethylether.** \( \text{C}_{11}	ext{H}_{14}	ext{O}_{2}(\text{O}_3) \), a thick syrup which puffed off on heating. Prepbd by Majima (Ref 2) by passing 6% ozone thru a cooled chloroformic soln of methyleugenol

**Triozonide des Eugenolmethylether.** \( \text{C}_{11}	ext{H}_{14}	ext{O}_{2}(\text{O}_3) \), a semi-solid, very expl compd. Prepbd by Majima (Ref 2), and then by Harries & Haarmann (Ref 3) by passing 15% ozone thru a cooled chloroformic soln of methyleugenol

**Refs:** 1) Beil 6, 963 2) R. Majima, Ber 42, 3668 (1909) 3) C.D. Harries & R. Haarmann, Ber 48, 40 (1915)

Naphthalene Diozone. \( \text{C}_{10}	ext{H}_{8}(\text{O}_3)_2 \), white crystls, very expl. It was first prepbd by Harries & Weiss (Ref 2), and again during WWII in the USA. It was found to be too sensitive and unstable to be used as an expl

**Refs:** 1) Beil 5, 540 & [444] 2) C.D. Harries & V. Weiss, Ann 343, 372 (1905) 3) V.I. Vaidyanathan, IndianJPhys 2, 427 (1928); Ibid, ChZtr 1928, II, 1757 & CA 22, 4349 (1928)

Phenanthrene Diozone. \( \text{C}_{14}	ext{H}_{10}(\text{O}_3)_2 \), colori crystls, very expl. Prepbd by passing ozone thru a cooled chloroformic phenanthrene soln


Phoronatediozone (Sym-Diisopropylideneacetonelozonide). \( \text{C}_{19}	ext{H}_{18}O_7 \), light green syrup, very expl, self-flammable on standing in air. Was prepbd by Harries & Turk by passing ozone thru a well cooled chloroformic soln of phorone \([2,4\text{-dimethyl-hexadien-(2,5)-on-(4)}]\), \((\text{CH}_3)_2\text{C:CH}_2\text{CO:CH}_2\text:C}(\text{CH}_3)_2\), followed by vacuum removal of chlf at 20°C

**Refs:** 1) Beil 1, 753 & (390) 2) C.D. Harries & H. Turk, Ber 38, 1634 (1905); Ibid, Ann 374, 349 (1910)

Pineneozonide and Pineneoxoaozone. A compn corresponding to something between \( \text{C}_{10}	ext{H}_{16} \) and \( \text{C}_{10}	ext{H}_{18} \) was obtained by Harries & Neresheimer (Ref 2) on treating right-rotary turpentine with weak ozone. It could be sep’d into thick oily (80–90% of the total) and solid fractions. The mixt was insol in common org solvents, and puffed off when heated on a spatula

The oily fraction was supposedly the ozonide, \( \text{C}_{14}	ext{H}_{14} \), bp 50°C at 15mm; d 1.31g/cc at 20/4°C; sol in org solvents except hexane; explods on heating

**Refs:** 1) Beil 5, 152 & (79) 2) C.D. Harries & H. Neresheimer, Ber 41, 38 (1908)

Polydihydrodiacyclopentadiene Ozonide. \( \text{C}_{10}	ext{H}_{14} \), white solid, mp 125–130°C, explods on heating. Sol in benz, CCl4, CS2; insol in eth and petr ether; decomps by w. Obtained by passing 5% ozone thru dihydrodiacyclopentadiene (Beil 5, [330])

**Refs:** 1) Beil 5, 331 2) H. Staudinger & H.A. Bruson, Ber 58, 1095 (1925)
Propylene-oxo-ozonide (C₃H₆O₄) and Propylene Ozonide (C₃H₆O₃). An exp oil, having a compn somewhat between these two compds, was prep by Harries & Haefner (Ref 2) by passing ozone thru an ethyl chloride soln of propylene, cooled in a mixt of solid CO₂—ether. This oil was very expl and possessed the following properties; d 1.1541 g/cc at 22/22°; RI 1.4034 at 22°.

When this oil was distilled in vac (18mm), the fraction collected between 28° and 34° corresponded almost exactly to the ozono-ozonide, C₃H₆O₄, d 1.070 g/cc at 22/22°; RI 1.3798 at 22°. It expld on heating with great violence. The residue of the distillation was also an expl, and it was assumed to be the ozonide, C₃H₆O₃. It was not analyzed by Harries et al.

According to Briner & Schnorf (Ref 3), propylene ozonide can be prep by passing ozone thru a soln of propylene in hexane, cooled to −80°. Briner & Meier (Ref 4) prep an expl compd by treating propylene in a dil gaseous phase with ozone, either in the presence or absence of H₂O, or in a non-aq solvent, as previously used by Harries et al.


α-Terpineol Ozonide. C₁₀H₁₈O₄, solid; sol in ether, benz and hexane; insol in petr ether. Was first prep by Harries (Ref 1), and then by Briner et al (Ref 2) by passing ozonized air thru a soln of α-terpineol in hexane.

This compd is one of the most stable among the ozonides. Its Q₀ is about 1500 cal/g, and the calc'd Q₀ is about 900 cal/g. It is only a mild expl.

In addition to α-terpineol ozonide, Briner et al prep and investigated other ozonides. Their conclusion was, that, although some of the ozonides are powerful expls, there is absolutely no advantage in employing them as commercial or military expls, because of their extreme sensitivity to impact and poor storage stability.

Refs: 1) Beil 6, (41) 2) E. Briner, M. Mottier & H. Paillard, Helv 13, 1030–5 (1930) & CA 25, 2137 (1931)

Toluene Ozonide. Colorful crystals or glutinous mass; stable at 0° but decomps at 8°; extremely expl. First prepd in 1891 by Dieckhoff.

Ref: C.D. Harries et al, Ann 343, 314 (1905)

Urushioldimethylethertherozonoinds

Urushiol is the liq secretion of Rhus vernicifera used in Japan lacquer. It contains an unbranched OH unsaturated side chain in the ortho position to the hydroxyl of pyrocatechol (Ref 3).

Urushioldimethyletherdiozonoide (Diozonid des Urushiol-dimethyläthers in Ger). C₂₂H₃₄O₂(O₃)₂, oily liq; expls on heating or by flame, but not as strongly as the tri- or tetraozonides, described below. Prep'd by Majima (Ref 2) by passing 6% ozone thru a chloroform soln of dimethylurhiol, cooled in ice, for 6 hours.

Urushioldimethylethertriozonoide (Triozonid des Urushiol-dimethyläthers in Ger). C₂₂H₃₄O₂(O₃)₃, light-yellow oily liq, expls on heating or on exposure to flame. Prep'd by Majima (Ref 2) by passing 6% ozone thru a chloroform soln of dimethylurhiol, ice cooled, for 16 hours.

Urushioldimethylethertetraozonoide (Tetra-ozonide des Urushiol-dimethyläthers in Ger). C₂₂H₃₄O₂(O₃)₄, yellow, semi-solid substance; expls violently when heated to about 60°, or when touched by a flame. Prep'd by Majima (Ref 2) by passing 15% ozone thru a chloroform soln of dimethylurhiol, cooled in ice, for 10 hours. After removal of the chlvr in vac, the residue was dissolved in ether and pptd by hexane.


Ortho-Xylene Ozonide. C₈H₁₀O₆ (probable structural formulae are shown in Ref 2). Colorful crystals. Was prep'd by passing 15% ozone thru a soln of o-xylene in acetic anhyd-ether, cooled to about
–25°. On pouring the resulting yellowish soln into ice-w, a ppt of the ozonide was obtained which proved to be very expl.

The ozonide can also be obtained using petr ether as the solvent for o-xylene. In this case, the ozonide ppt separates during ozonization, because it is insol in petr ether. An expln can occur during removal of the ppt from the ether. For this reason, Levine & Cole (Ref 2) considered it more convenient to use acetic anhyd as solvent for o-xylene.

"P" (Explosifs de mine). Older Fr mining expts which were also used for military purposes. Typical of these were No 1: AN 80, Guncotton 20%; No 2: AN 90.5, Guncotton 9.5%. Ref: Daniel (1902), 595


"P" (Pebble Powder). Blk Pdr in the form of cubes, used by the Brit Army until 1876, and later replaced by EXE Powder (see Vol 6, E348-R). Refs: 1) Daniel (1902), 595 2) Marshall 1, 29 (1917)

P-2. Designation for 50/50 cast Pentolite charge Ref: Cook (1958), 251-L

PA. Abbreviation for Picric Acid

"P.A." Explosives. A variety of expl blends, patented by the firm of Bombrini-Parodi-Delfino of Rome, consisting of PETN desensitized with pentaerythritol acetate. These expts can be cast below 100°, are less sensitive to shock than PETN, but more sensitive than TNT. Although they are less powerful and brisant than PETN, they are more so than TNT. Their stability is less than that of TNT. Their advantage in comparison with RDX formulations lies in the uniformity of the blend Ref: Vivas, Feigenspan and Ladreda 2 (1946), 288–9

"P.A." (Poudre). Prismatic BlkPdr used by the Fr at the end of the last century Ref: Daniel (1902), 595

Packaging of Ammunition and Explosives

The term Packaging can be defined in a military sense as including preservation, packaging, packing, marking (see in this Vol, M18-L), and omni-transport loading of ammo and expts (Refs 4–7, 24–26, 29a, 29b and 31–33). A non-military definition also includes minimum overall costs plus the concept of product advertising as being included in the marking of the packages (Refs 8 and 18). Under either aegis (military or civilian), packaging must satisfy five divergent sets of requirements as stated in developed guide lines covered in the indicated references and articulated by the appropriate Mil Specs. These requirements represent a compromise between the goals of the manufacturer, who would like to minimize overall costs and increase efficiency by using packaging machinery wherever possible; the ammo design engineer, who would like ease of use of the item ("ready-for-use in the package" concept), and the relative advantages of either environmentally degradable or reusable containers; the transportation specialist, who would like a rugged, shock and vibration resistant package of convenient size and minimum wt which can be palletized and handled by fork lift truck; the safety engineer, who would like not only an omnisafe, fire and vibration resistant package, but one that can be ventilated and conveniently undergo surveillance for deterioration in storage; and the user, who would like a package with easy access requiring only simple hand tools, of limited wt, sabotage-proof, tamper-proof, theft-proof, with a 10-yr storage life under adverse environmental and weather conditions over temp ranges of from −80°F to 160°F, easily identifiable contents, and being amenable to camouflage (Mi) and accurate record keeping (Refs 4, 6, 15–18, 29 and 36).

In order to comply with all of the objectives which have been stated above, plus international, Federal, state and local regulations, a concerted effort has been made to evolve new packaging materials, new packaging techniques, and to develop new containers (Refs 1–4, 8–10, 12, 14–23, 25–30 and 32). [See also "Loading and Fabrication of Explosives" in Vol 7, L46-L to L57-L]. These efforts have resulted in an applied packaging technology outlined below for selected ammo and items and expts:
Ammunition For Artillery usually consists of a complete round packaged in strong wooden, especially designed plastic or metal containers (Refs 29a, 29b, 33 and 34)

Ammunition For Small Arms (Mil) is packaged in strong wooden or metal containers. Within these containers it may be loose, in bandoleers, in magazines (clips), or in belts of 200 rounds. The gross wt of the outside container must not exceed 175 lbs (Refs 17, 33 and 34). Civilian purpose small arms ammo is usually packaged in polyethylene or polyurethane foam cushioned cardboard boxes of from 20 to 50 rounds. A number of these boxes are then over-packaged in a larger cardboard box. The content of the larger box varies with the type of ammo packaged, ie, 50 boxes of rifle ammo, 25 boxes of shotgun ammo, and 2000 rounds of pistol ammo (subdivided in boxes of from 20-50 rounds depending on the round caliber). The popularity of .22 cal ammo is such that transparent plastic containers are used with individual cavities for 100 rounds per box (Ref: Interviews with the store managers of both "Dover Sport", Dover, NJ and "Lester Edelman’s" of Wayne, NJ on June 14, 1976)

Explosive Bombs, Mines, Projectiles, Torpedoes or Grenades. If the item exceeds 90 lbs in wt and 4.5 inch diam it may be securely fastened to a pallet. Other items are secured in strong wooden or metal boxes (Refs 33 and 34)

Fireworks (Pyrotechis). These devices are usually packaged in fiber boxes or drums of net over 65 lbs gross wt. If wooden boxes are used gross wt is not to exceed 150 lbs. For many types of individual items “tin” cans, fiberboard boxes, or self-contained special prepacking is used. Packaging is usually limited to 150 boxes per over-box (Refs 33 and 34)

Fuzes and Tracers are individually wrapped in pasteboard or plastic tubing. No more than 50 of these individual packets are to be in the next outer, usually pasteboard, carton. Special provisions are made for securing individual packages of fuzes or tracers against movement. The over-pack container is a strong, tight wooden or fiberboard box. Gross wt of a wooden or triple wall fiberboard box is not to exceed 150 lbs, and of a fiberboard box, 65 lbs (Refs 30, 33 and 34)

High Explosive Gels (up to 30% liq expi) are contained in cartridge casings or shells of polyethylene-paper; a small number being placed in grease-proof paper bags. These bags are contained in wooden boxes with liq expi absorbative sawdust or cellulose sheet linings (Refs 33 and 34)

High Explosive Liquids. Strong metal containers of 10 quart capacity are used with wooden box overpacking (Refs 33 and 34)

Solid High Explosives such as TNT or Pentolite are packaged in fiber drums (200 lbs gross wt), or in wooden boxes over strong paper or cloth bags (100 lbs gross wt) (Refs 33 and 34)

Initiating High Explosives such as LA or LSt are packaged with 20 to 40% w or an antifreeze mix of ethanol/w in a 4 oz duck bag, which is then overwrapped with a strong grain bag. The outer container is a metal barrel or drum. The dry wt of the expi is not to exceed 150 lbs (Refs 33 and 34)

Nuclear Weapon Major Assemblies are packaged for shipment in accordance with the applicable service technical manuals; viz, Army-TM’s (Technical Manuals) (Ref 35), Navy-SWOP’s (Special Weapons Operational Procedures), and Air Force-TO’s (Technical Orders), etc.

Liquid Propellants can be packaged in 12 gallon polyethylene drums inside of strong, tight metal drums (Refs 33 and 34)

Solid Propellants are packaged, for example, in tight metal drums, gross wt not to exceed 200 lbs (Refs 33 and 34)

Rocket Ammunition with Explosively Loaded Projectiles are packaged, for example, in specially designed preformed fiberglass resin impregnated or Al containers (Refs 33 and 34)

Written by H. L. HERMAN

Refs: 1) Anon, “Rules For Handling, Storing, Delivering, and Shipping Explosives”, Inst of Makers of Expls, Pamphlet No 5, NY (1939)
2) Anon, “Regulations Governing Transportation of Military Explosives on Board Vessels During Present Emergency”, NAVCG 108, Wash, DC (1945)
3) Anon, “Explosives or Other Dangerous Articles on Board Vessels”, USCG 187, US Govt Printing Off, Wash, DC (1950)
6) Anon, “Ammunition Packing De-

Paléine or Paléina. Dynamites patented by Langfrey in Engl in 1878 contg nitrated straw (“fulmi-paille”). One of the formulations contd: NG 35.0, Nitrostraw 18.6, saltpeter 32.5, sulfur 4.6, and potato starch 9.3%. Part of the sulfur could be replaced with hardwood charcoal, and dextrin could be substituted for the starch.

These Dynamites were stable and fairly insensitive to shock. Incorporation of hydrocarbons rendered them still less sensitive, and suitable for military purposes.
Palmer’s Explosive. AN or AP 50, DNT 14, Na or K nitrate 31, and paraffin wax (mp > 120°) 5%. For a quicker expl, the proportions used are 70, 13 and 7%, respectively.

Refs: 1) W.H. Palmer, BritP 20214 (1909) & CA 3, 2507 (1909) 2) Ibid, USP 990585 (1911) & CA 5, 2332 (1911)

Panclastites (see also under Anilite or Anulithe in Vol 1, A443-R). Liq expls of the Sprengel type, patented in France by Turpin in 1881, contg liq N₂O₄ as oxidizer and CS₂ as fuel. Later, petroleum, benzol, toluene, xylenes, aniline, mixts of CS₂ and NB, naphthols, pitch, and vegetable and animal oils were also proposed as fuels. Some of these substances were nitrated (Ref 8).

Panclastites were inexpensive and easy to prepare, and were very powerful, some possessing a greater brisance and higher detonation velocity than either TNT or PA.

All the Panclastites were extremely sensitive to shock, and for this reason the ingredients could not be mixed in advance and transported to the work site. Mixing had to be done just prior to use, this being a major disadvantage in their utilization. In addition, N₂O₄ is a corrosive liq, and requires special vessels for its transportation.

Following are examples of some of the most commonly used Panclastites:
1) Liq N₂O₄ 64.3, CS₂ 35.7% by wt. Decomp on expln as follows: 2CS₂+3N₂O₄ → 2CO₂+4SO₂+3N₂. Some characteristics, as given in Ref 5 are: “force specifique” 6455 vs 8910 for TNT; abs temp of expln in °K, 3731 vs 3423 for TNT; vol of gas developed by 1 kg of expl, w calc as vapor, at 760mm and 0°, 4599 vs 6888 for TNT. According to Stettbacher (Ref 4), it has a Trauzl test value (power) of 330cc vs 305cc for PA, and a crusher test value (brisance) of 3.3mm vs 3.05 for PA.
2) Liq N₂O₄ 81.8, benz 18.2% by wt. Decomp on expln, according to A. Pérez Ara (Ref 7), as follows: C₆H₆+3N₂O₄ → 3CO₂+3CO+3H₂O+3N₂
3) Liq N₂O₄ 69.8, NB 30.2% by wt. Decomp on expln as follows: 8C₆H₃NO₂+25N₂O₄ → 48CO₂+20H₂O+29N₂. According to Stettbacher (Ref 4) this mixt has a d of 1.38g/cc, heat of deton of 1777cal/g, vel of deton of 8000m/sec, is more brisant (crusher test value 5.05mm vs 4.9mm) and more powerful (Trauzl test value 505cc vs 490cc) than NG or even Pentrit (50/50 PETN/NG). According to Pascal (Ref 2) the vel of deton of a 65/35 N₂O₄/NB mixt is 7650m/sec.
4) Liq N₂O₄ about 68, 65/35 NB/CS₂ about 32% by wt. This mixt gave a Trauzl test value of 432cc and a crusher test value of 4.3mm, vs 490cc and 4.9mm for NG, respectively.

Panclastites were tested in the 1880’s by the Ger navy in marine torpedoes. For this, two thick, sealed glass vessels, one contg N₂O₄ and the other CS₂, were placed in each warhead. The set-back forces produced on firing a torpedo broke both vessels, resulting in the formation of an expl mixt which was detonated by an impact fuze when the torpedo reached the target. Although the results of the trials were favorable, Panclastites were not adopted by the Ger navy because of the inconvenience of handling the ingredients, and the danger of premature breakage of the glass vessels in the warhead.

Although Panclastites are very powerful and brisant expls, their use was very limited (even as commercial expls), and with the appearance of many new expls at the end of the last and beginning of the present century, their use was discontinued. They were, however, resurrected during WWI, because of the shortage of such conventional expls as TNT, PA, DNB, TNB, Nitronaphthalenes, etc., and used extensively in weapons which had just begun to come into vogue, namely, “aeroplane drop bombs”. Fr used Panclastites under the name “Anilite” (qv) in a specially designed bomb with two compartments. Italy also seems to have used Panclastites (N₂O₄-benz) to some extent, since, in 1921 or 1922, they experienced an expln at Brodico involving 4500kg of N₂O₄ and 1500kg of benz (Ref 5).

Panclastites were even used in WWII, in some of the heaviest Brit aircraft bombs (Fliegerbomben in Ger). These bombs had two compartments, as described under “Anilite” [Ref 2 (1948)].
Pandasticites-Guhr. In order to avoid the problems inherent in using liq expl ingredients, Turpin, in 1881–82, invented exps in which the N₂O₄ was absorbed by guhr (see Vol 8, G174-L) or other materials. Such “solid” N₂O₄ was mixed with either a solid fuel or a liq fuel absorbed on a solid compd.

Refs: 1) M. Turpin, FrP 146497 (1881) & 147676 (1882)  2) Daniel (1902), 598

Pandora. A WWII code name for the Long Aerial Mine, which consisted of an expl charge attached to 2000 ft of cable. The object of this RAF innovation was to tow the charge behind a Havoc aircraft and train it in the path of Ger bombers. It did not prove successful, and the idea was abandoned in November 1941.


Pannonit. An Austrian pre WWI permissible low-freezing mining expl contg NG 25.5, NC (collodion cotton) 1.5, AN 37, dextrin 4, glycerol 3, MNT 5, & Na or KCl 24%. It was fired with a special detonator contg TNT, and replaced the previously used “Progressit” (qv)

Refs: 1) Anon, SS 8, 398 (1913)  2) Marshall 1 (1917), 398  3) Naoum, NG (1928), 417

Pantopolit. An older Dynamite, manufd at the end of the last century by the Rheinische Dynamit Gesellschaft at Opladen, near Kölén, Ger. It contained NG dissolved in naphthalene 67–70, guhr 20–23, Ba sulfate 7 & chalk 3%. The naphthalene content was to increase the gas vol produced on expl

Refs: 1) Daniel (1902), 599  2) PATR 2510 (1958), Ger 122-R  3) Giua, Trattato II (1) (1959), 345

Panzerfaust. A Ger WWII antitank projectile weapon utilizing a shaped charge expl and a tungsten carbide core. It was lighter than an earlier version (Panzerschreck), and could be handled by one person. Its trajectory was flatter than the Panzerschreck, with a range of 150 meters.


Panzergranate. Ger for a WWII projectile used against armor plate, or an AP (armor-piercing) projectile. According to Stettbacher (Ref), they were of one piece construction with a solid, sharp nose. They were effective against softer armor, but not against hardened steels.

Ref: Stettbacher (1948), 401

Panzerschreck. A Ger WWII weapon, similar to the American Bazooka. It fired an 88mm projectile, which was about 50% larger than the Bazooka, but its trajectory was more curved and its range shorter. Two persons were required to operate the weapon. Later in the war, the rocket size was increased to 100mm. This resulted in better penetration, but made the weapon too heavy to use, and it was superseded by the Panzerfaust.

Ref: L.E. Simon, “German Research in World War II”, J. Wiley, NY (1948), 188

Panzerwurfkanone. A Ger smooth-bore 80mm mortar developed during WWII by Rheinmetall for firing hollow-chrg projectiles at longer ranges than the Panzerschreck or Panzerfaust. It fired an 18-inch finned projectile weighing 6 lbs at a muzzle velocity of 1700 fps to an effective range of 700 meters. The projectile penetrated 140mm of armor at a 60° angle of impact.

Ref: L.E. Simon, “German Research in World War II”, J. Wiley, NY (1948), 188
Paper Chromatography, Paper Partition Chromatography. See under Chromatography in Vol 3, C289-L to C298-L

Papers, Explosive. See under Explosive Papers or Pyropapers in Vol 6, E424

Papita. Fr designation for acrolein (see Vol 1, A96-L), used during WWII in some artillery shells and gas grenades. It was intended to serve as a powerful lachrymator which contained neither bromine nor acetone, both being in short supply in Fr during this period. Its toxic effects were comparable to phosgene
Ref: C. Wachtel, "Chemical Warfare", Chemical Publishing Co, NY (1941), 168–70

Paraffin (Paraffin wax, Hard paraffin). A mixt of solid hydrocarbons having the general formula C\text{n}H\text{2n+2}, obtained from petroleum. Color or white; somewhat translucent, tasteless, odorless solid; greasy feel; burns with a luminous flame. D 0.880–0.915 g/cc, mp 47–65°, flash p 390°F, autoignition temp 473°F, non-toxic (Refs 8 & 9)  
Insol in w, alc and acids; sol in benz, chlf, eth, ligl, turpentine, CS\text{2} & oils; miscible when melted with wax, spermactei & fats (Refs 8 & 9)  
The use of paraffin in the expl industry is extensive, not only as a moisture protecting agent, but as a desensitizer. Paraffin can be incorporated either directly with ingredients of expl comps (at a temp above its mp), or one or more ingredients can be coated separately with molten paraffin and then mixed. When hygroscopic substances, such as AN, Na nitrate, etc, are coated in such a manner, they are rendered less hygroscopic, and, when the same procedure is applied to sensitive comps or expls (K chlorate, RDX, PETN, etc) their sensitivity can be markedly reduced  
One of the first to use paraffin in expls was A. Nobel, who incorporated small quantities in some of his Dynamites  
In the 1880's, the Fr prep'd and tested a series of "paraffined nitrocelluloses" (Refs 1 & 2). Several mixts were prep'd by incorporating various amts of paraffin (5 to 20%) into hot, wet NC, followed by extrusion into cartridges and drying. It was found that while mixts contg 5% paraffin could be detonated with a cap contg 1.5g of MF, mixts with 10% or more paraffin required a "cartouche-amorce auxiliaire" (booster). Cartridges contg 5% paraffin burned without detonation on bullet impact. Cartridges of NC desensitized with paraffin were used extensively in Europe as late as WWI for demolition purposes  
H. von Bezdol (Ref 3) details many uses of paraffin in the expls industry, and gives methods of analysis as well  
In addition to being used in many commercial expl comps (such as Cheddites, Minsite Explsifs, Gesteins-Koronisit, etc), paraffin has been used for military purposes. Paraffined AP in the compn AP 86, paraffin 14% was used in Fr in 75mm artillery shells, but was found to be too sensitive, causing prematures. It was, however, suitable for loading mortar shells, hand grenades and aircraft bombs. As an example, the following mixt was used for loading 58mm trench mortar rounds: AP 61.5, paraffin 8.5 & Na chloride 30% (Ref 6, p 366)  
Paraffin is also used for impregnating paper used for cartridgeing expls, as well as moisture proofing paper cartridges already loaded with hygroscopic Dynamites  
In the pyrot area, paraffin is widely used in the manuf of book and wooden matches, as a protective coating to counteract possible surface deterioration of metal powders, as a lubricant and waterproofing agent for the interior surfaces of kraft paper flare and signal cases, and as a binder which tends to fill interstices between particles on press loading (Ref 7, pp 69, 71, 302 & 316)  
A US Federal Specification, "Wax, Paraffin, Technical", VV-W-95A (31 May 1968) contains requirements for procurement of this material. It covers two types and six grades of paraffin wax:  
Type I – Fully Refined  
Grade AA – mp 145–150°F  
Grade A – mp 125–140°F  
Grade B – mp 130–134°F  
Grade C – mp 123–127°F  
Type III – White Crude Scale  
Grade B – mp 124–128°F  
Grade C – mp 118–122°F  
The min-max mp ranges for each grade are
deted by the cooling curve method described in ASTM Standard D87-66

Color (Iiq), Saybolt: Type I, +25 min; Type I, Grade AA, +23 permitted; Type II, no requirement. The procedure is described in ASTM Standard D156-64, "Saybolt Color of Petroleum Products"

Oil content, %, as described in ASTM Standard D721-85T, "Oil Content of Petroleum Waxes":

<table>
<thead>
<tr>
<th>Type</th>
<th>% Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade AA</td>
<td>0.5</td>
</tr>
<tr>
<td>Grade A</td>
<td>0.5</td>
</tr>
<tr>
<td>Grade B</td>
<td>0.5</td>
</tr>
<tr>
<td>Grade C</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Workmanship: The finished wax shall be clean, homogeneous in appearance, and free from dirt and other foreign matter

Refs: 1) Commission des Substances Explosives, MP 1, 468 & 483–4 (1882–3); Ibid, 2, 386–7 & 605 (1884–89); Ibid, 5, 73 (1892)
2) Daniel (1902), 600 3) H. von Bezdol, NC 3, 119–21 (1932) & CA 28, 4954 (1932)
4) A. Stettbacher, NC 7, 181–3 (1936)
9) CondChemDict (1971), 657-L

Nitroparaffins, Explosives Derived From. Although mononitroparaffins are generally not expl, they can be used for the prep of expls

Aaronson (Ref 1) nitrated nitroisobutylglycerin to Nitroisobutylglycerintrinitrate, 2-nitro-2-methyl-1,3-propane diol to 2-Nitro-2-methyl-1,3-propane diolinitrate, and 2-nitro-2-methyl-1-propanol to 2-Nitro-2-methyl-1-propanolinitrate. Their prep and characterization follow:

Nitroisobutylglycerintrinitrate, O₃N.C(CH₂ONO₂)₃, mw 286.14, N 19.58%, OB to CO₂ 0%

Preparation of Nitroisobutylglycerin. Several procedures for the preparation of this compd are given in the literature. Of those tried, that described by Stettbacher [Nitrocellulose 5, 162 (1934)] gave the best results. The method of prep follows:

Into a three-necked, 1-liter reaction flask set into a water bath placed on a hot plate were added 150g of Nitromethane (Eastman Kodak No 189 — Distillation Range 98–101°) and 2g of K carbonate (K₂CO₃, ½H₂O). A total of 675g of 37% formaldehyde of reagent grade were slowly added. The formaldehyde content was determined by oxidizing to formic acid in a measured amt of standard alkali soln and titrating the excess alkali (See Scott's Standard Methods of Analysis, 5th Ed, p 2149). Addition of the formaldehyde raised the temp, and the rate of addition was adjusted and the cooling bath regulated so that the temp was maintained below 30°, until about 200g of the formaldehyde had been added. The heat of reaction was then permitted to raise the reaction mixt to about 80°, while the remainder of the formaldehyde was added in about one-half hour and then heated at about 90° for two hours. The yellowish soln was concd under reduced press (about 4 inches). It smelled strongly of formaldehyde. Water was added and the soln again concd as before to remove some of the formaldehyde. Dilution and concn were again repeated. On cooling an almost solid mass of crystals, reeking strongly of formaldehyde, separated. This red colored mass was filtered, but filtration was very slow due to the viscous sticky character of

Refs: 1) Davis (1943), 276 & 289 2) CondChemDict (1971), 657

Paraffin Oil (Mineral Oil, Liquid Petrolatum). Colori, tasteless, transparent liq, consisting mostly of liq paraffin hydrocarbons; bp 330–390°, d 0.84–0.94/gcc. Inisol in w, cold alc and glycerin; sol in eth, chlf, CS₂, benz, petr eth, gasoline & boiling alc

It is obtained by distn of high-boiling petroleum fractions, followed by purification. The latter operation consists of treatment with concd sulfuric acid, then concd Na hydroxide soln, and filtration thru decolorizing carbon. In order to reduce the solid paraffins, the oil is chilled and filtered

Paraffin oil has been used in several Nitrostarch blasting expls (Ref 1, p 276), as well as in some smokeless powders, for example, in "bulk sporting powders". A typical compn is NC (12.90% N) 87.00, K nitrate 6.0, paraffin oil 4.0, Ba nitrate 2.0, and diphenylamine 1.0% (Ref 1, p 289)
the filtrate. After several hours, the mass was dissolved in hot alc and recrystallized. By repeated recrystals from ether there was finally obtained material melting at 165° and above. The various mother liquors were similarly recryst in order to accumulate sufficient material for nitration.

Preparation of Nitroisobutyglycerininitratate. The procedure followed was that given by Stettbacher, [Nitrocellulose 5, 183 (1934)]. 50g of the nitrobutylglycerin were gradually added with mechanical stirring to 304g of a mixed acid having the composition sulfuric acid 60%, nitric acid 38%, and water 2%. The temp was maintained below 15° by means of a cooling bath and the acid added in about ½ hour. The mixt was stirred for an additional ½ hour, during which the temp fell to +5°. After transferring to a separatory funnel and allowing the mixt to stand for awhile, the heavier spent acid was drawn off. The residual product was washed with water, then with Na bicarbonate soln until it was alkaline, and then with water to neutrality to litmus (2 washes). The washings were added to the separated spent acid, extracted thoroughly with ether, the ether extract washed with water to neutrality and then added to the main separated product. The ether was removed from the product by evaporating and then drying in a vacuum desiccator. A yield of 95% of the theoretical was obtained. The nitrate nitrogen was determined by the nitrometer and gave a result of only 14.02%. The product was renitrated exactly as above except that the temp was held at just below 20° for 1 hour. After extraction with ether, washing and drying as above, the nitrate nitrogen was raised to 14.12%.

Using the material thus obtained, a number of tests and determinations were made with the results given in Table 1. The Drop Test, de-

<table>
<thead>
<tr>
<th>Property</th>
<th>Nitroisobutylglycerininitratate</th>
<th>Nitroglycerin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate nitrogen, %</td>
<td>14.07 (theory 14.68)</td>
<td>18.50 (theory)</td>
</tr>
<tr>
<td>Drop Test, 2 kg wt</td>
<td>25 cm</td>
<td>44 cm</td>
</tr>
<tr>
<td>Temp required for decomposition in secs</td>
<td>185° without detonation</td>
<td>—</td>
</tr>
<tr>
<td>Sand Test, sand crushed by 0.2g [a]</td>
<td>28g</td>
<td>30g</td>
</tr>
<tr>
<td>82.2° KI Heat Test</td>
<td>2 minutes</td>
<td>Specification minimum</td>
</tr>
<tr>
<td>Effect of flame when sealed in capillary tube</td>
<td>Detonation</td>
<td>15 minutes Detonation</td>
</tr>
<tr>
<td>Volatility at approx 25°:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss in g per sq cm per 24 hrs</td>
<td>0.127 x 10⁻³</td>
<td>0.153 x 10⁻³</td>
</tr>
<tr>
<td>Freezing point</td>
<td>Below —50°</td>
<td>About +12°</td>
</tr>
<tr>
<td>Refractive Index (D line)</td>
<td>1.4896 at 25°</td>
<td>1.4713 at 25°</td>
</tr>
<tr>
<td></td>
<td>1.4874 at 30°</td>
<td>1.4693 at 30°</td>
</tr>
<tr>
<td>Gelatinizing action on Nitrocellulose</td>
<td>Slight</td>
<td>Strong</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Slight, decidedly less than NG</td>
<td>Very marked</td>
</tr>
<tr>
<td>Soluble in</td>
<td>Methyl and ethyl alcohols,</td>
<td>Most organic solvents</td>
</tr>
<tr>
<td></td>
<td>acetone, ether, ethylene-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dichloride, chloroform</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and benzene</td>
<td></td>
</tr>
<tr>
<td>Insoluble in</td>
<td>Water, carbon disulfide,</td>
<td>Water (practically insol)</td>
</tr>
<tr>
<td></td>
<td>petroleum ether</td>
<td>petroleum ether</td>
</tr>
</tbody>
</table>

[a] When absorbed by 0.2g of kieselguhr
composition temp, and the 82.2° KI Heat Test were made according to procedures standard at PicArsn. In order to determine the brisance value of the Nitroisobutylglycerininitrate, it was mixed with an equal weight of kieselguhr and 0.4g of the mixt hand pressed into the detonator cap. The volatility at approx 25° compared with NG was determined by exposing approx equal wts of the materials in similar dishes to the air and weighing daily for a number of days. The refractive index was determined by means of an Abbé refractometer over the range 24—33°. Whether the compd had any gelatinizing action on NC was determined by adding a few drops to a small amt of NC and mechanically working to determine whether or not gelatinization had taken place.

A study of the results showed that Nitroisobutylglycerininitrate was a powerful exp of the same class as NG, but that it was much more sensitive to impact and much less stable, as judged by the 82.2° KI Test. Stettbacher [Nitrocellulose 5, 203 (1934)] reported the low stability of this material, but attempted to minimize this important defect by ascribing the low heat test values to long drying at 40—60° in order to remove the ether. In this work, the ether was removed by a current of air at room temp and then by holding the exp under reduced pressure in a vacuum desiccator until there was no further loss in weight. In spite of those precautions very low 82.2° Heat Test values were obtained. Its gelatinizing action on NC was too slight to permit the use of Nitroisobutylglycerininitrate as a solvent unless large quantities were employed. Aaronson (Ref 1) concluded that it was too unstable to be of military value.

2-Nitro-2-methyl-1,3-propanediolinitrate.

\[ \text{NO}_2 \]
\[ \text{CH}_3\text{C(CH}_2\text{ONO}_2)_2, \text{ mw 225.14, N 18.67%, OB to CO}_2 -24.87\% \]

Purification of 2-nitro-2-methyl-1,3-propanediol. This material was purchased from the Commercial Solvents Corp and had a melting point of 135—136°. By recrystallizing twice from 95% alc the mp was raised to 151.2°. This purified material was used for nitration.

Preparation of 2-Nitro-2-methyl-1,3-propanediolinitrate. 50g of the dry ground diol prepd above was sifted into a mixt of 300g of a mixed acid having the compn nitric acid 40% and sulfuric acid 60%, while the mixt was mechanically agitated and the temp maintained at about 15°. After the addition, the temp was allowed to rise to 20° and maintained for ½ hour. After standing for an hour, the mixt was transferred to a separatory funnel and the spent acid drawn off. The residual oily liq was washed twice w/ warm (about 45°) aq Na sulfite soln and then with warm distd w until neutral to litmus. The liq was dried in a vacuum oven at 50°, and then chilled. A milk white waxy mass was obtained, yield 76.0% of theory. The properties of this material were obtained and the results shown in Table 2. The washings were added to the spent acid and the whole extracted thoroughly with ether. The ether extracts were combined, washed w/ w, evaporated and dried to constant wt in a vacuum desiccator. Yield 16.2% of theory, which made a total nitration yield of 92.2%.

<table>
<thead>
<tr>
<th>2-Nitro-2-methyl-1,3-propanediolinitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate nitrogen</td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>Drop Test, 2 kg wt</td>
</tr>
<tr>
<td>Temp required to cause decompn in 5 secs</td>
</tr>
<tr>
<td>Sand Test, sand crushed by 0.4g</td>
</tr>
<tr>
<td>82.2° KI Heat Test</td>
</tr>
<tr>
<td>Gelatinizing action on Nitrocellulose</td>
</tr>
<tr>
<td>Toxicity</td>
</tr>
<tr>
<td>Soluble in</td>
</tr>
</tbody>
</table>

a When initiated by 0.24g of Mercury Fulminate and 0.08g of Tetryl
The 2-nitro-2-methyl-1,3-propanediol purified by recryst was of high purity as indicated by its melting point of 151.2°, which compared with 150° reported by Vanderbilt and Hass [Ind & Eng Chem 32, 36 (1940)]. Nitration of the above compd yielded 2-Nitro-2-methyl-1,3-propanediolinitrate in 92% total yield as a milk-white waxy solid melting at 37.4°. It was an expl with a brisance value about equal to that of Tetryl. However, it was very sensitive to impact, having a Drop Test value of only 11 cm with a 2-kg hammer. This was not in agreement with the statement by J.A. Wyler [USP 2195551 (1940)] to the effect that it was very insensitive to impact and that a “10 kg weight dropping 100 cm does not cause a detonation.” Like the other nitroparaffins, 2-Nitro-2-methyl-1,3-propanediolinitrate showed very poor stability in the 82.2° Heat Test even after repeated and careful stabilization. It had practically no gelatinizing action on Nitrocellulose. Aaronson (Ref 1) concluded that it was too unstable to be of military interest.

2-Nitro-2-methyl-1-propanolinitrate.

\[ \text{NO}_2 \]
\[ \text{CH}_3 \cdot \text{C} \cdot \text{CH}_2 \cdot \text{ONO}_2, \text{mw 164.14, N 17.07\%, OB to} \]
\[ \text{CH}_3 \]
\[ \text{CO}_2 - 68.23\% \]

Purification of 2-nitro-2-methyl-1-propanol. Material melting at 86–87° and made by the Commercial Solvents Corp was recryst from benzene and dried in a vacuum desiccator. The mp was about 88° (not sharp). This material was used for nitration.

Preparation of 2-nitro-2-methyl-1-propanolinitrate. 50g of the 2-nitro-2-methyl-1-propanol purified as above were slung into a mixt of 58.5g of 90.5% nitric acid and 241.5g of 103.1% sulfuric acid (oleum) while the well-agitated mixt was maintained close to 15°. Stirring was continued for 1 hour and the mixt allowed to stand for 1/2 hour. No separation of the nitration product occurred and the mixt was poured over cracked ice. An oily layer separated. The mixt was transferred to a separatory funnel, washed with water, Na bicarbonate, and twice with water to neutrality. The separated diluted spent acid together with the washings were thoroughly extracted with ether; the ether extract washed to neutrality and added to the main product. The ether was removed by evaporation and the residue dried in a vacuum desiccator. The yield was 34.8g or 50.5% of the theoretical. Table 3 gives the results of the tests made on this material.

<table>
<thead>
<tr>
<th>Properties of 2-Nitro-2-methyl-1-propanolinitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>16.99%</td>
</tr>
<tr>
<td>(theory 17.07%)</td>
</tr>
<tr>
<td>Drop Test, 2 kg wt</td>
</tr>
<tr>
<td>100+ cm</td>
</tr>
<tr>
<td>Temp required to cause decompn</td>
</tr>
<tr>
<td>200–205° without detonation</td>
</tr>
<tr>
<td>in 5 secs</td>
</tr>
<tr>
<td>Sand Test a</td>
</tr>
<tr>
<td>Not detonated by 0.35g of Lead</td>
</tr>
<tr>
<td>Azide and 0.2g of Tetryl, or by 0.5g of Mercury</td>
</tr>
<tr>
<td>Fulminate</td>
</tr>
<tr>
<td>82.2° KI Heat Test</td>
</tr>
<tr>
<td>6 minutes</td>
</tr>
<tr>
<td>Gelatinizing action on Nitrocellulose</td>
</tr>
<tr>
<td>Toxicity</td>
</tr>
<tr>
<td>Similar to Nitroglycerin</td>
</tr>
<tr>
<td>Soluble in</td>
</tr>
<tr>
<td>Alcohol, ether, acetone, benzene, and CCl₄</td>
</tr>
<tr>
<td>Insoluble in</td>
</tr>
<tr>
<td>Water and petr ether</td>
</tr>
</tbody>
</table>

Test charge consisted of 0.2g of 2-nitro-2-methyl-1-propanolinitrate absorbed by 0.2g of kieselguhr.

2-nitro-2-methyl-1-propanol was obtained in good quality by recryst from alc. The mp of the material used, 88°, should be compared with 89.5–90.0° given in the literature [Ind & Eng Chem 32, 36 (1940)]. On nitration 2-nitro-2-methyl-1-propanolinitrate was obtained in about 50% yield. It was not detonated by the fall of a 2 kg hammer from a height of 100 cm, and was insensitive to initiation by strong detonating agents. It caused headaches similar to those caused by Nitroglycerin, and it was a good gelatinizing agent for Nitrocellulose. However, like the other nitroparaffin derivatives discussed above, it was quite unstable, giving a very low 82.2° Heat Test value. It, therefore, was considered to be unsuitable for military use (Ref 1).

Blatt (Ref 3) gives the following additional test data for this compd from other sources:
Impact Sensitivity. 2 kg at 100 cm gives 0/2 shots

Power. 75% of blasting gelatine by Ballistic Mortar

Stability. 82.2° KI Heat Test, 4 and 8 minutes (two sources)

Remarks. Gelatinizes blasting soluble Nitrocotton rapidly at room temp

In a final summary report on the prepn of Nitroparaffins (Ref 2), the following compds were synthesized: Tetranitromethane; 1,1-Dinitroethane; 1,2-Dinitroethane; Hexanitroethane; 1,1-Dinitropropane; 2,2-Dinitropropane; 2,2-Dinitrobutane; 2,2-Dimethyl-1,3-dinitropropane; 2,2,3-Trinitrobutane; 2,2,3,4-Tetranitrobutane; 2-Methyl-2,2,3-trinitrobutane; 2,2-Dimethyl-2,3-dinitrobutane; 2-Methyl-2,3,3-trinitropentane; 3-Methyl-2,2,3-trinitropentane; and 3-Ethyl-2,2,3-trinitropentane. However, it was concluded that none possessed properties satisfactory for military exps. This disqualification generally resulted for the following reasons: 1) low mp or high vap press, 2) those compds contg α-hydrogens were strongly acidic, and 3) certain arrangements of nitro groups were thought to be inherently unstable

The following compds could not be synthesized: 1,1,1-Trinitropropane; 1,3-Dinitrobutane; 2,3-Dinitrobutane; 2-Methyl-1,1,2-trinitropropane; 2,2-Dimethyl-1,1,1-trinitropropane; 2,2-Dimethyl-1,1,3-trinitropropane; 1,3-Dinitro-2-methyl-2-(nitromethyl) propane; 2,2-Dimethyl-1,1,3-tetranitropropane; 2,2,2,2,2-Dimethyl-1,1,3,3-tetranitropropane; 2,2,2,2-Dimethyl-1,1,3,3-tetranitropropane; 3,3-Dimethyl-1,1,3-trinitrobutane; 2,2,5,5-Tetranitrohexane; 3,3,4,4-Tetranitrohexane; 2-Methyl-2,3,3,4-tetranitropentane; 3-Methyl-2,2,2,2,4-pentanitropentane; 3,3,4,4,3-Tetranitrohexane; 2,2,2,2,3,4,4,4-3-Methyl-2,3-trinitrohexane; 2,2-Dimethyl-1,4,4,4-trinitropentane; 2-Ethyl-1,2,3,3-trinitropentane; 3,3-Dimethyl-2,2,2,4,4-tetranitropentane; 2,3,3-Dimethyl-1,4,4,3,3-trinitrohexane; 2,5-Dimethyl-2,3,3,4,4,5-hexanitrohexane; 3,4-Dimethyl-2,2,3,4,5,5-hexanitrohexane; and 2,2,4,4,4-Tetras (nitromethyl) pentane. Ref 2 details a listing of a variety of methods attempted in these unsuccessful syntheses

The above Ref also lists reactions which either succeeded or failed to yield poly-nitroparaffins, salts of methazonic acid and polynitroparaffins, nitroolefins and their polymers, nitrates of nitrohydroxy compds, and nitrated alcohols

Written by S. M. KAYE


Paraformaldehyde. \((\text{CH}_2\text{O})_n\), mw \((30.03)_n\); white, crys powder; mp 64°, bp sublimes, range of polymerization n=8 to 100. Note: Paraformaldehyde is not the same as sym-trioxide, which melts at 150–60°. Slowly sol in cold, more readily in hot w, with evolution of formaldehyde; insol in alc & eth; sol in fixed alkali hydroxide solns. Obtained by concentrating formaldehyde soln. At ordinary temps, it gradually vaporizes, yielding formaldehyde gas

Paraformaldehyde Explosives.

When paraformaldehyde is treated with hydrogen peroxide, expl compds, similar to those obtained by treating formaldehyde with \(\text{H}_2\text{O}_2\) (methyl hydrogen peroxide or dimethyl peroxide) are obtained. According to Bamberger and Nussbaum (Ref 2), mixts of solid paraformaldehyde and 60% \(\text{H}_2\text{O}_2\) are brisant expls which detonate on heating or under the influence of a blasting cap. This mix detonates spontaneously when left in contact with Pb for a short time, presumably from the heat generated by the oxidation of the Pb. Expl crysts of mp 50° were sep from paraformaldehyde-peroxide mixts. See also under Formaldehyde Polymers and Formaldehyde and Derivatives (Explosives Obtained Therefrom) in Vol 8, F164-L to F167-L

Paragón. Mix of K perchlorate 60, nitro compds 10, sawdust or cereal flour 20, Na chloride 6, and powdered Zn-Al alloy 4%. Ref: A. Pérez Ara (1945), 218.

Paraldehyde. See under Acetaldehyde and Derivatives in Vol 1, A14.

Paradal. See under Acetaldehyde and Derivatives in Vol 1, A15-R.

Parammons (Parammons). Perchlorate expls used by the Fr during WWI for loading aerial bombs:

<table>
<thead>
<tr>
<th></th>
<th>No I</th>
<th>No II</th>
<th>No III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate, %</td>
<td>86</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>Paraffin, %</td>
<td>14</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

Of these, No II had an OB to CO₂ close to zero, and its power by Trauzl test was 4700cc. It was about as sensitive to impact as the Ched-dites, and could be expld by rifle bullet. According to Stettbacher (Ref 3), mixt No II was used again during WWII for military purposes Refs: 1) Naoům, Exps (1927), 135 2) Stettbacher (1933), 316 3) Stettbacher (1948), 91.

Paraplex. A trademark for a group of alkyd type polymeric materials known as polyester resins. These resins are primarily long chain polybasic acids esterfied with polyhydric alcohols such as glycol sebacate, glycerol, or ethylene glycol. Some are oil-modified while others are unmodified polyesters. Paraplex resins are manufd by Rohm & Haas Co, Phila, Pa.

Some Paraplex resin mixts, such as Paraplex P-10 containing Paraplex resin AP-31 and styrene, are used by the Aerojet Engrg Corp, Azusa, Calif as an ingredient of JATO propints (see below). The same resin has been used as a constituent of resin-bonded expls (also, see below), while still other Paraplex resins are used to fabricate ceramic-faced composite armor (Ref 4 Refs: 1) L.H. Eriksen, "Study Stability and Sensitivity Characteristics of Paraplex Propellant", PATR 1628 (1946) 2) E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR 2062 (1954) 3) H.F. Mark, Ed, "Encyclopedia of Polymer Science and Technology", Vol 11, J. Wiley, NY (1964), 129-168 4) J.E. Gubierz & L.E. Day, "Development of Reinforced Plastic Backing for Ceramic-Faced Composite Armor (U)", PATR 3226 (C) (1965).

Paraplex P-10. One of the P-series of Paraplex resin mixts which contain resins such as Paraplex Resin AP-31 together with varying amounts of styrene to form soins of unsaturated polyesters. Paraplex P-10 contains a 50/50 mixt of Paraplex Resin AP-31/styrene. It is a thermosetting mixt but can also be cured at RT (or higher using steam) with a peroxide catalyst such as benzoyl peroxide to either a flexible, semi-rigid, or rigid compd. It finds use in low pressure laminating, casting and molding applications. Specific military applications for Paraplex P-10 are in expls as a binder with RDX (see below), and in propints as a liner compn with asbestos fiber (Ref 1), and as a fuel with KClO₄ (see below) Refs: 1) W.E. Campbell Jr., "Report No 1 on Restricted Propellant Charges Containing Paraplex Resin Fuel", Aerojet Engrg Corp, Azusa, Calif, Report No 183, Contract NOa (S) 5350 (1946) 2) E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR 2063 (1954) 3) CondChemDict (1971), 658.

Paraplex Propellants. A series of JATO propints (the PF-series) developed by the Aerojet Engrg Corp, Azusa, Calif using Paraplex P-10 resin-styrene mixt as a fuel ingredient in the amt of approx 26.5%. Other ingredients are AN or K perchlorate, 73.0%, and small amts of t-butylhydroperoxide or benzoyl peroxide, 0.1 to 0.5% (as a polymerization catalyst) (Ref 2)

The Paraplex propints have a specific impulse of 199 lb/(lb/sec) at 2000 psia chamber press. They exhibit great thermal stability above 150°F and great impact strength at -20°F. Measured parameters of interest (KClO₄ content, PF-6 Propult): A loading d of 1.86g/cc; an expln temp of 600°; a friction pendulum test of 10 unaffected in 10 trials using a steel shoe; Q₆ 965cal/g; an impact test using PA apparatus with

Paraplex Resin-Bonded Explosive. Usually consists of Paraplex P-43/RDX/Al/Styrene monomer/Lupersol DDM (as a polymerization catalyst) in the following percentages, viz.; 60/65.0/20.0/9.0/0.5. Density 1.65 g/cc. The material is mixed and polymerized using the usual procedure for polyester resins and Plastic Bonded Exps (see in this Vol)

The following parameters were measured for the above formulation. A brisance of 71.6 g sand crushed; a deton rate of 7921 m/sec; an expln temp of 280°; a friction pendulum result of 3 partial deton in 10 trials using a steel shoe; a 100° heat test result of no weight loss in 48 hrs and no expln in 100 hrs; an impact sensy of 17 inches in a PA appr using a 2 kg wt (TNT=14-15 inches), and 5.3 ft in a BurMines appr at the 50% pt using a 2 kg wt (TNT = 11.2 ft); power by BalMort of 119 (TNT=100), and by Trauzl test of 157 (TNT=100); a rifle bullet impact test of 1 sample flashed, 3 smoked and 1 unaffected out of 5 trials; a sensy to initiation of 0.300 g LA; an excellent storage stability (wet and dry storage plus JAN-cycles); and a vac stability of 0.25 ml after 40 hrs at 100° Ref: E.T. Benning, "Development of Resin-Bonded Explosive Compositions", PATR 2062 (1954)

Paravane. A protective underwater device, invented during WWI by C.D. Burney of the Brit Navy, which, when towed with a wire rope from a fittig on the bow of a ship, rides out from the ship's side and cuts the cables of anchored mines. The mines will then rise to the surface, where they can be seen and destroyed. Another version, called "explosive paravane" contains an expl charge which is towed at some distance from a vessel. If a submarine is suspected of being nearby, the charge is detonated electrically Ref: J. Quick, "Dictionary of Weapons and Military Terms", McGraw-Hill, NY (1973), 340

Parazol. A mixt consisting mainly of p-dinitro- and o-dinitro-dichlorobenzenes, N 11.8%, yellowish crysts, mp 63—85°, cast d 1.694g/cc. It can be prepbd by the nitration of commercial dichlorobenzene. Parazol is nearly insol in w; very difficulty sol. in cold alc; easily sol in hot alc; sol in eth, benz and CS₂.

It is an expl, less powerful, brisant and sensitive than TNT. Its thermal stability is satisfactory (Abel Test 65.5°, 60 minutes; German Test at 135°, 120 minutes). Parazol does not ignite at temps as high as 340°. When hand packed, it compresses a Pb block 27% vs 39% for TNT

The power of Parazol, as detd by Cope (Ref 1), is about 86% of TNT (Bal Mort Test, consisting of detg the quantity of Parazol required to cause deflection equal to the deflection from 10g of TNT). It is less sensitive to detonation than TNT and, when confined, requires a very powerful detonator

According to Davis (Ref 6), the chlorine in dinitrochlorobenzene is active, while that in monochlorobenzene is unreactive. It yields dinitrophenol by hydrolysis, dinitroaniline by reaction with ammonia, and dinitromethylaniline by reaction with methylamine. These and similar materials may be nitrated to produce expls, because introduction of a third nitrogroup is done very easily after the chlorine has been replaced by a more strongly ortho-para orienting group. Tetryl, as well as hexanitrodiphenylamine, have been produced starting with dinitrochlorobenzene

Parazol was used in Europe during the early days of WWI for filling projectiles. According to Davis (Ref 6), this was done because of a shortage of toluene, necessary for the manuf of TNT; an abundance of chlorine, produced during
manuf of caustic soda by an electrolytic process; and the ready availability of benz.

In order to utilize the chlorine, large amts were used for the chlorination of benz to produce chlor- and dichlorobenzenes, used at that time as insecticides and moth exterminators. At the same time, attempts were made to nitrate the dichlorobenzene, which proved to be expl. When mixed with TNT in HE shells, it did not detonate completely, but presented interesting possibilities because the unexploded portion, atomized in the air, was a vigorous itch-producer and lachrymator, and because the exploded portion yielded phosgene.

After WWI, Babcock (Ref 2) patented a mix similar to Parazol for use in military expls. PA can be incorporated in such mixts. Toxocity. The crude material is more toxic than the purified. The crude material, when applied to the human skin for 2 hours, produced hyperemia and finally small vesicles, which developed into blisters contg a clear fluid after 48 hours. After 4 days, the latter started to heal. The dust and fumes were also toxic, and the irritant action of the fumes increased with temp (Ref 5)


Paris Guns. See under Big Bertha, Paris Gun and Other German Big Guns of WWI and WWII in Vol 2, B113-R

Parkes' Absorbent for Nitroglycerin. Materials patented in 1898 by Parkes, manufd by Chemische Fabrik at Winkel-on-Rhine, Ger, for use in Dynamites as absorbents for NG in lieu of the previously used kieselguhr. The absorbents were rubber-like materials, prep'd by the action of sulfur chloride, S₂Cl₂, on vegetable oils. It was claimed at the time that Dynamites prep'd with Parkes' absorbent were so insensitive, they could be used for loading shells. The absorbents could also be used for coating sensitive expls such as MF, PA, etc. For this, the powdered expl was mixed with a soln of Parkes' absorbent, and then gradually dried to eliminate the excess solvent.

See also under Bielefeld's Gelatinization Method in Vol 2, B113-L and Chemische Fabrik Dynamites in Vol 2, C178-R

Ref: Daniel (1902), 134

Parlon (Chlorinated Rubber, Tornesit, Allopren). A proprietary trade name (Hercules Powder Co) for a rubber chlorinated polyisoprene, CH₃

[-CH₂=CH=CH₂]ₓ, chlorinated approx 67% Cl by wt. A white coarse amorph inelastic or poorly cryst granular powder; mp 140° (softening point of film); d 1.56g/cc (solid), also given as 1.64g/cc and up. Sol in CCl₄, esters, aromatic hydrocarbons and ketones; insol in acet; unaffected by strong or weak acids or alkalis, salt spray, aliphatic alcs and hydrocarbons.

The chlorination of rubber results in a complete reaction. There is not only addition and substitution of chlorine, but also cyclization along the polymer chains. The theoretical chlorine content for the completely chlorinated isoprene unit, C₅H₈Cl₄, is 68.5%. Parlon is marketed in five viscosity types. Stabilized Parlon usually contains 1% of an epoxy compd as a stabilizer to improve resistance to heat, ultraviolet light and moisture. Sunlight causes discoloration and embrittlement in unpigmented, unstabilized films. Parlon is resistant to dampness, soaps, molds and mildew.

Parlon is nontoxic and nonflammable. It will ignite in the flame of a bunsen burner, but the flame is self-extinguishing. On burning, it melts, giving off bubbles of gas and chars.

Parlon has been used in pyrotechnic tracer formulations as a color intensifier and binder (Ref 4). It is also employed as a base for rapid drying concrete paints and alkyd enamels (Ref 5)

Parone Explosive. A mixt consisting of 2p K chlorate and 1p CS₂ prep'd consisting in Italy at the end of the last century. On its first exptl firing in a 240mm mortar, it burst the mortar tube.
Refs: 1) Cundill (1889) in MP 6 (1893)
2) Daniel (1902), 601 3) A. Pérez Ara (1945), 206

Parr Calorimeter (Parr Bomb). A device invented by S.W. Parr in 1912, and improved since then by the Parr Instrument Co of Moline, Illinois. It can be used to detn the heats of combustion of energetic materials by burning them with oxygen under pressure. Exptly, a weighed sample is ignited in an O₂ atm by an electrically heated wire in a closed combustion chamber or “bomb”. The heat evolved during combustion is absorbed by a weighed quantity of water surrounding the combustion chamber. By observing the temp rise of the water, and knowing the energy equivalent of the calorimeter, the amt of heat released from the sample can be calc'd (Ref 3)

It should be noted that, prior to Parr, other calorimeters existed which used oxygen under pressure for combustion in closed vessels, namely, those of Berthelot (1881) and its modifications and variations, Berthelot-Vieille, Moreau, Landrieu-Malsaléz, and of the “Commission des Substances Explosives”. Later bombs were those of Mahler (1892), Attwater (1899) and Kast (constructed at Chemisch-Technische Reichsanstalt, New-Babelsberg, near Berlin, Ger).

Parr not only improved the design of the above existing bombs, but reduced their cost by variations in mechanical details and by the use of new materials for the combustion chamber.

See also under Calorimeter, Calorimetry and Calorimetric Determinations in Vol 2, C10-L to C12-R.
Refs: 1) Vennin, Burlot & Lécorché (1932), 62–66
3) Anon, Fisher Scientific Co Catalog 74 (1974), 73

Parrott Gun. A type of muzzle-loading cast-iron rifled gun with a wrought-iron band shrunk around the breech for extra strength. It fired cylindroconical projectiles including shot, shell, case shot, and canister. Guns of this type, in calibers ranging from 2.9 to 10 inches, were used in the US Civil War era. They were invented by an American, R.P. Parrott.

Particle Size Effects in Detonation. The raison d'être for particle size effects in detonations was clearly stated many years ago in the following quotation from Eyring (Ref 1):

“All solid explosives in actual use are composed of grains. These grains may range in size from a few microns upward to single crystals some centimeters across. The granular structure is sometimes produced intentionally by milling the explosive, but even cast explosives are granular polycrystalline materials, as may easily be seen under the microscope or inferred from the fact that the density of cast explosives is below the single-crystal density.”

At first glance, it might be supposed that the granular nature of an explosive would be of no significance, that the high temperature in the detonation wave would first vaporize all the explosive, which would subsequently react according to the kinetic laws for homogeneous reactions. But this is not so. In the short time during which the explosive grain is exposed to the high temperature (a microsecond, more or less) the heat is unable to penetrate deeper than the surface layers. Consequently, each grain of explosive begins reacting at its hot surface, and the reaction progresses layer by layer until it reaches the center of the grain. The reaction for each grain within the reaction zone of a detonation is thus a sort of “cigarette burning”, in which one layer of molecules is not ignited until the previous layer is consumed.

This grain-burning theory is supported by two kinds of arguments: the first from the impossibility of heat conduction through a grain, and the second from the experimentally observed effect of grain radius on the reaction time.”

Eyring et al then deduced the following eqns:
The time $\tau$ required for complete reaction is merely the time required for the reaction to traverse the grain radius $R_g$:...
\[ \tau = \frac{1}{kr} \frac{Rg}{\lambda} \]  

(1)

Since the extent of reaction \( N = 1 - (R/R_g)^3 \), the rate law for grain-burning becomes:

\[ \frac{dN}{dt} = \frac{3kr}{R_g} \lambda (1 - N)^{2/3} \]  

(2)

where \( kr \) is the specific reaction rate (reciprocal mean life) for one molecule and \( \lambda \) is the molecular diameter. If grain-burning occurs in the detonation process, then according to Eq 1, the reaction time \( \tau \) of such a process should be proportional to \( R_g \) the grain radius of the expl. There is a considerable body of circumstantial evidence that this is indeed the case (Refs 1, 8, 12, 13 & 15). Some of this evidence will be discussed below.

Regardless of any theory, there is firm exptl proof that the particle size of a granular expl affects its steady detonation properties as well as its initiation behavior. In particular, the detonation velocity as well as the critical diameters of many granular expls depend on their particle size. The shock sensitivity of granular expls is also influenced by particle size. These effects will now be described.

Steady Detonation.

Fig 1 (presented by Cook in Ref 3 for TNT at a bulk density of about 1 g/cc) shows that at a given diameter the detonation velocity, \( D_c \), decreases as \( R_g \) increases. Note, however, that particle size effects disappear at larger column diameters.

For the more "sensitive" expls like PETN, the influence of particle size effects on \( D \) are much less pronounced that for TNT (unpublished work by the writer and Ref 2).

The critical diameter, \( d_c \), of many "insensitive" granular expls increases with increasing particle size. This is shown in Fig 2 for TNT and the following tabulation for Picric Acid and for Ammonium Perchlorate.

---

Fig 1. Theoretical versus Experimental D(d) Curves for TNT

Fig 2. Critical diameter of TNT as a function of initial density. 1. Pressed or powder after Andreev and Belyaev (1960) (Ref 6).
Grain size: (a) 0.01–0.05mm; (b) 0.07–0.2mm
Initiation Phenomena.

A common test for the sensitivity, ie, the initiation susceptibility, of an expl is the detn of the minimum priming charge required to produce detonation. Baum et al (Ref 4) present the following tabulation to show that the min priming charge for several aromatic nitro cmpds decreases with their decreasing particle size.

<table>
<thead>
<tr>
<th>Name of Explosive</th>
<th>Min charge of Lead Azide, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For particles passing thru a sieve with 2500 holes/cm²</td>
</tr>
<tr>
<td>Trinitroxylenol</td>
<td>0.34</td>
</tr>
<tr>
<td>Trinitrobenzene</td>
<td>0.19</td>
</tr>
<tr>
<td>Trinitrotoluene</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Fig 3. Effect of Compaction on Predetonation Column Length of Tetryl. (□ 20µ, ○ 470µ)

In initiating PETN by sparks generated by a condenser discharge, Romanov & Sten’gach (Ref 14) found that discharge energies for 50% expln increased with increasing PETN particle size. Similar effects are reported for several other expls (see Vol 5, E43).

The effect of particle size on DDT (deflagration-to-detonation) transition is complex. Andrews & Chiu (Ref 7) claim that the pressure above which PETN combustion becomes unsteady and accelerates decreases with increasing PETN particle size. Other studies suggest that there is an optimum particle size for DDT (see Sect VII of Propellants, Solid in this Vol). In a recent study, Bernecker et al (Ref 16) found that at a given degree of compaction, 20-micron Tetryl had a longer run-up to detonation, than 470-micron Tetryl. This is shown in Fig 3. Exploding bridgewire initiation of PETN was studied by Blackburn & Reithel (Ref 9). They observed that transition to detonation is aided by fineness (actually increased specific surface) of the PETN particles.

Probably the most studied initation phenomenon is that of impact initiation (see Vol 7, I35-R). Particle size does not appear to influence the impact sensitivity of granular expls. There is some evidence, however, that decreasing particle size makes impact more reproducible.

Several studies have shown that the shock sensitivity of granular expls depends on expl particle size. The consensus is that the threshold shock pressure to initiate detonation in a given expl is less for large particles than for small particles. However, the converse is true when one considers run-up distances (or run-up times) to detonation. Thus at some pressure above the threshold for both large and small particles, run-up to detonation is smaller for small particle charges than for large particle charges.

The above effects were observed for Tetryl by Seely (Ref 8); for RDX by the writer (Ref 12); for PETN, RDX & Tetryl by Scott (Ref 13); and for RDX & TNT by Dravin & Shvedov (Ref 15). The latter used a novel technique to demonstrate that small particles, once initiated, attain steady detonation more readily than larger particles. Their results for RDX are summarized in Fig 4. The insert graph shows the measurement method used, wherein u, the particle velocity, is observed as a function of time t.
Fig 4. (From Dremin & Shvedov, Ref 15)

Blackburn & Seely (Ref 11) recorded the light given off during detonation of granular expls. They found that for coarse Tetryl or PETN, light was produced in discrete bursts whose dimensions were roughly equivalent to the dimensions of the interstices of the granular charges.

To summarize, the particle size of a granular expl influences both its initiation and steady detonation behavior. Grain-burning provides an explanation for some of these effects. However, the lower shock threshold or discrete detonation for coarse-grain expls cannot be explained in terms of grain-burning. Possibly, as suggested by Seely (Refs 8 & 11), the operative mechanism in the latter is some form of flow stagnation.

Written by J. ROTH


PARTICLE SIZE MEASUREMENTS OF SOLID PROPELLANTS,EXPLOSIVES, AND PYROTECHNICS

The term “particle” and “particle size” are so highly ambiguous as to require precise definition. As used in this article “particles” will be limited by size to those distinct entities which have physically detectable boundaries in any direction within the limits of 0.05 and $10^4$ microns (1 micron, $\mu = 0.001$ mm). This size range covers those particles which can be directly measured without magnification down to those which exhibit colloidal behavior.

The performance characteristics of solid expls, proplns, and pyrots, depending as they do on surface reactions, are strongly influenced by the size of the component particles. If a particle is a sphere its size is uniquely determined by its diameter in microns. Only rarely are powdered materials composed of spherical particles because on crushing or grinding, a laminated or bedded material always tends to produce slabs, monoclinic crystals tend to produce acicular particles, while isometric crystals tend to produce cubicle particles. Crystal form tends to be preserved regardless of fineness of subdivision of individual particles. If a particle is non-spherical the size is usually regarded as an equivalent spherical diameter (ESD), i.e., the diameter of a sphere with the same volume as the non-spherical particle. Such a measurement is not always convenient to make; accordingly, the diameter of a circle whose area is equal to the projected area of the particle is generally the dimension used to express the sizes of irregular particles. This is the projected area diameter (da). These diameters are conveniently measured in the microscopic range (0.2 to 5.0 $\mu$ diameter) with the ocular micrometer (graticule) invented by Patterson and Cawood (Ref 3). The graticule consists of a rectangle and a series of ten numbered circles and
corresponding discs engraved on glass. When inserted in the focal plane of a (X12) compensating microscope eyepiece, the rectangle, circles, and discs appear super-imposed on the field of view of the microscope. If a deposit of particles to be measured is placed on a microscope slide and properly focused in the field of the microscope, the images of the particles contained within the rectangle can be rapidly matched by eye against the discs or circles and their sizes determined from the parameters of the microscope and the known dimensions of the graticule. It is recommended that the deposit be so dispersed on the microscope slide that the number of particles observed within the rectangle averages about 6, and no particles overlap. The optical measuring technique is thus a fairly precise, absolute method of measuring particle size.

When all the particles of a system are composed of the same-sized particles the system is mono-disperse, whereas different-sized particles compose polydisperse particle systems. The occurrence of monodisperse particle systems is rare, polydisperse particle systems are the most common. Thus, the particle sizes of any material are associated with their frequency of occurrence and a particle size distribution which can be determined by some form of particle size analysis.

The frequency of occurrence may be reported either as the number of particles or as the weight greater than or smaller than a stated range of sizes (Ref 38).

Two methods for representing size distributions graphically are given in Fig 1. The frequency distribution plot gives the fraction of particles (on whatever basis is desired) that lie in a given narrow size range as a function of the average size of the range (or of some function $\Psi(D)$ of the average size). The lower curve of Fig 1 is a cumulative distribution curve, the integral of the frequency curve. Being an integral, the method of choosing size increments need not be selected or specified.

The shape of a frequency distribution curve will depend on how the size increments were chosen. With the common methods for specifying increments, the curve will usually take the general form of a skewed probability curve with a single peak. However, it may also have multiple peaks, as in Fig 2. There are various analytical relationships for representing size distributions. One or the other may give a better fit of data in a particular instance. There are times, however, when analytical convenience may justify one. The log-probability relationship is particularly useful in this respect.

Fig 1  Frequency and Cumulative Distributions of Size

Fig 2  Comparison of Unimodal and Bimodal Distributions
The log-probability frequency distribution is given by Eq (1):

\[
d\phi_x \propto \frac{1}{D/D_{m\text{x}}^{\frac{1}{2}} \exp \left\{ \frac{-\ln(D/D_{m\text{x}}) \sigma}{\sqrt{2} \ln \sigma} \right\}}
\]

with \( \phi_x \) = the cumulative fraction smaller than size \( D \) on a basis corresponding to \( x \); \( D \) = the particle diameter; \( \sigma \) = the standard geometric deviation; and \( D_{m\text{x}} \) = median diameter on the basis of a property corresponding to \( x \).

The values of \( \sigma \) and \( D_{m\text{x}} \) are characteristic constants for a given size distribution. If a material follows a log-probability distribution on one basis (\( x \)), it also does on any other basis (\( y \)) — with the same value of the standard geometric deviation \( \sigma \) but a different value of median size \( D_{m\text{x}} \) corresponding to the new basis \( y \). This is a unique property of log-probability distribution (See Eq 2):

\[
D_{m\text{x}} = D_{m\text{y}} \exp \left[ (x-y) \frac{\ln^2 \sigma}{2} \right]
\]

A graph paper based on this type of relationship can be obtained. It permits convenient graphical representation of size distribution data (as shown in Fig 3) even if the distribution does not follow a log-probability relationship. In addition, the assumption of a log-probability distribution as an approximation permits simple conversion from one basis of representing size distribution, mean size, or median size to another basis.

The solid line typifies the shape of curve shown by actual materials on this type of plot. If a material obeys a log-probability relationship, the plot on this graph paper is a straight line, as shown by the two dashed lines, and can be completely characterized by two numbers: (1) a median diameter, corresponding to the 50% cumulative size, and (2) a standard geometric deviation, a number equal to or greater than unity that is the ratio of the 84.13% to the 50% or the 50% to the 15.87% cumulative size.

The median diameter is a measure of the general size level, whereas the standard geometric deviation is a measure of the degree of uniformity. A completely uniform material (all particles the same size) would show up as a horizontal line in Fig 3 and have a standard geometric deviation of 1.0. A completely heterogeneous material would be represented by a vertical line which would have a standard geometric deviation of infinity.

Most materials will tend to approximate log-probability distributions at the fine end (usually with standard geometric deviations in the range of 2 to 3) and to level off at some upper limiting size, as indicated by the solid curve. Approximating the data by a straight line either in the fine range or over the entire range may, at times, be expedient because of the ease with which certain properties of the material can be ascertained analytically.

Before beginning a size determination, it is customary to look at the material, preferably under a microscope. This examination reveals the approx size range and distribution of the particles, and especially the shapes of the particles and the degree of aggregation. If microscopic examination reveals that the ratios between max and min diameters of individual particles do not exceed 4, and indirect technique for particle size distribution based on sedimentation or elutriation may be used. Sedimentation techniques for particle size determination were first used by Hall (Ref 2) in 1904. He showed that the ratio of fall of individual particles in a fluid was directly related to the particle size by the hydrodynamic law derived by Stokes from Newton's law of fluids in 1849 (Ref 1). This basic equation of the motion of a particle suspended in a fluid assumes that when subjected to constant driving force the particle acceleration is opposed by the
resistance of the fluid to motion. In Stokes Law as usually stated, the force of resistance to motion \( F \) of a sphere is:

\[
F = 6 \pi \eta vd
\]  

(3)

where \( d \) is the diameter of a sphere, \( \eta \) is the viscosity of the fluid, and \( v \) is the velocity of the particle. Although Stokes' Law is strictly applicable only to spherical particles, it has been shown by Irani and Callis (Ref 26) to apply to particles whose max-to-min-diameter ratio does not exceed 4 with only small error. When applied to non-spherical particles settling under the driving force of gravity, particle diameter in equation (3), \( d \), is replaced by the Stokes diameter, \( d_{st} \), which is the particle diameter averaged over all possible orientations of the particle. In addition, particles smaller than 200\( \mu \) settling in a viscous medium almost instantaneously reach a terminal velocity at which point the driving force (gravity) becomes equal to the resistance:

\[
\frac{\pi}{6} d_{st}^3 \left( \rho_1 - \rho_2 \right) g = 6 \pi \eta v d_{st}
\]  

(4)

where \( \rho_1 \) and \( \rho_2 \) are the densities of the particle and the suspending medium respectively, and \( g \) is the acceleration of gravity, which in turn reduces to:

\[
d_{st} = \left( \frac{18 \eta v}{\left( \rho_1 - \rho_2 \right) g} \right)^{1/2}
\]  

(5)

For particles smaller than 2 microns, settling times under gravitational forces become extremely long and subject to errors because of Brownian movement, so that in such cases centrifugal sedimentation must be employed. Stokes' equation holds strictly only at extremely slow motion in the hydrodynamic region of laminar or streamline flow (for Reynolds' number \( \leq 0.1 \)). The critical upper limit of particle size analysis by sedimentation is 63\( \mu \) when \( w \) is the suspending medium. By using suspending media such as dioctyl phthalate the critical diameter may be increased up to about 3500\( \mu \).

For size analyses of particles larger than \( \sim 63 \mu \), the geometric properties of uniformly constructed physical barriers such as sieves are commonly used. Though this technique of finished product size control dates back to at least 2500 BC when the Egyptians constructed woven cloth sieves for preparation of foodstuffs, it is only within the last 100 years that such devices were actually standardized for size analysis.

No single method of size analysis is entirely satisfactory for application to the entire range of particle size exhibited by energetic materials. The choice of method from available resources depends largely upon the properties of the material to be analyzed, the basic significance or physical wearing of the measurement, and the purpose for which the information is required. For example, failure to disperse the particles as discrete entities is the biggest single problem in all size analysis methods that depend on individual particulate behavior. With microscopic techniques particles must be dispersed on the slide to permit observation of individual particles, and in sedimentation techniques the material must be suspended in the fluid so that the particles behave as individuals and not as flocs. In sedimentation or in “wet” sieving, the fluid medium chosen must be a dispersant as well as a non-solvent for the particles being analyzed. Most size measurement techniques do not measure size. They usually measure some phenomenon that is markedly, but not solely or uniquely, determined by size. To illustrate, in sedimentation analysis the discriminating property is the terminal settling velocity. In one type of sedimentation analysis particle concen as a function of time is measured (Ref 38). The concen measurement may be made either by gravimetric, or turbidimetric means; in the first case, yielding results on a mass basis while in the second, results are on a surface basis. There is a choice of methods available for particle size analysis (Table 1), and the following details of the methods which have been applied to energetic materials indicate what particular methods can or cannot achieve, as well as the limitations of the data that are generated.
Table 1
PARTICLE SIZING TECHNIQUES
AND RANGES

<table>
<thead>
<tr>
<th>DIRECT</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(microns)</td>
</tr>
<tr>
<td>1. Microscopy</td>
<td></td>
</tr>
<tr>
<td>a. Visible light</td>
<td>0.2-100</td>
</tr>
<tr>
<td>b. Electron beam</td>
<td>0.001-5</td>
</tr>
<tr>
<td>2. Coulter Counter</td>
<td>10-1000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INDIRECT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sieving</td>
<td>44 and up</td>
</tr>
<tr>
<td>2. Sedimentation</td>
<td></td>
</tr>
<tr>
<td>a. Liquid</td>
<td></td>
</tr>
<tr>
<td>(1) Pipette</td>
<td>2-50</td>
</tr>
<tr>
<td>(2) Hygrometer</td>
<td>2-50</td>
</tr>
<tr>
<td>(3) Manometer</td>
<td>2-50</td>
</tr>
<tr>
<td>(4) Balance</td>
<td>2-50</td>
</tr>
<tr>
<td>(5) Turbidimeter</td>
<td>2-50</td>
</tr>
<tr>
<td>(6) Centrifuge</td>
<td>0.05-50</td>
</tr>
<tr>
<td>b. Gas or Air</td>
<td>2-150</td>
</tr>
<tr>
<td>3. Elutriation</td>
<td></td>
</tr>
<tr>
<td>a. Air</td>
<td>5-50</td>
</tr>
<tr>
<td>b. Air and centrifuge</td>
<td>2-50</td>
</tr>
<tr>
<td>4. Permeability</td>
<td>1-1000</td>
</tr>
<tr>
<td>5. Adsorption</td>
<td></td>
</tr>
<tr>
<td>a. Liquid phase</td>
<td>0.01-5</td>
</tr>
<tr>
<td>b. Gas phase</td>
<td>0.01-5</td>
</tr>
<tr>
<td>6. Light scattering</td>
<td>0.05-1</td>
</tr>
</tbody>
</table>

DRY SIEVING OR SCREEN ANALYSIS
WOVEN WIRE SIEVES

Sievings is probably the easiest and certainly
the most popular method of size analysis but is
restricted to powders having the greater portion
coarser than 75 \( \mu \). For finer powders the method
is limited by the high cost of producing sieves
with uniform, small apertures

A sieve is an open container, usually cylindrical,
having definitely spaced and uniform openings
in the base. The openings are square when
wire or filter mesh is used and may be circular or
slit shaped when the openings are formed by
punching holes in a metal plate

If a series of sieves is stacked in order of
increasing mesh size, when a known amount of
powder to be analyzed is placed on the topmost
sieve and agitated, the powder will then be classi-
fied on the individual sieves into fractions in
accordance with the size of the particles and the
size of the openings. Sieving takes place at the
clear if and when: a) a fine particle is located
above a vacant mesh; b) the cross section of the
particle is smaller than the width of the mesh;
and c) a force in terms of time and magnitude is
present which moves the particle out of the
material-to-be-screened and thru the mesh

A closed pan, a receiver, is placed at the bot-
tom of the stack of sieves to collect the fines,
and a lid is placed on top to prevent loss of
powder; agitation may be manual or mechanical.
Results are usually expressed in the form of a
Cumulative under size percentage. The compar-
atively simple procedure of screening some-
times leads to the assumption that it most prob-
ably provides unequivocal results. This is a fallacy
attested to by the in-depth investigations by
Whitby in the USA (Ref 7) and Batel in Germany
(Ref 9). Industrially, most sieving is accom-
plished by the steady-state approach in which particu-
lar material is fed continuously at a constant
clearing into a sieving machine and the amount and
quality of the material passing and the residue
are measured. However, in the laboratory and
for test purposes, the far simpler non-steady-
state approach is used. In the usual procedure, a
known quantity of the particulate material is
placed on a screen or a stack of graded series
screens and sieved by hand or in a mechanical
device such as either a RO-TAP or an End-
Shake (Ref 21) and the amount and quality of the particulate passing or retained as a function
of time or per impact is measured

Whitby (Ref 7) discovered that in the non-
steady-state with mechanical sieve shakers, the
percentage passing versus sieving time curve
could be divided into two regions with a transi-
tion between (Fig 4). Region 1 exists when there
are many particles much less than the mesh size
still on the sieve, while region 2 exists when the
residue on the sieve consists entirely of near-
mesh or larger particles

Region 1: It was further discovered that with
mechanical sieving the rate at which material
passes the sieve in region 1 is very nearly con-
stant and obeys the following relationship:

\[
\text{Percent passing} = at^b
\]

where:  \( t \) = sieving time

\( b \) = a constant very nearly equal to 1

\( a \) = a sieving rate constant
Further investigation revealed that the sieving rate constant was a function of several variables:

\[ aW = C_1 \rho N S^3 \left( \frac{S}{k_s d_m} \right)^{1/n} \sigma_{gp} \] (7)

where:  
- \( W \) = Total load on sieve  
- \( \rho \) = Particle Density  
- \( S \) = Mesh opening  
- \( t \) = Sieving time  
- \( k_s d_m \) = Geometric mass mean of the particle size distribution  
- \( N \) = Total number of mesh openings in sieve  
- \( \sigma_{gp} \) = Geometric standard deviation at a particular particle size on the size distribution curve  
- \( C_1 \) = Log-Log intercept of \( aW/\rho N S^3 \) at \( S/k_s d_m = 1 \)

**Characteristics of Region 1 (High Load) Sieving:**  
a) Effect of load depth on sieve: Particle interaction influencing sieving rate extends only about 1 mesh opening above sieve; and b) the sieving rate is inversely proportional to the mean particle size for a given ratio of mesh opening to mean size  

**Effect of Material and Load:** The sieving constant, \( C \), increases geometrically with load. In addition there is a shape factor, a roughness factor, and a density factor such that:

\[ C = F_s V R_s \] (8)

where:  
- \( R_s \) = a surface roughness factor  
- \( F_s \) = a shape factor  
- \( V \) = \( w/\rho \)

\[ P = \frac{dN}{Nd(\log t)} = \frac{\log \sigma_{gp}}{\log \sigma_{gt}} \] (9)

where:  
- \( P \) = probability  
- \( N \) = the number of particles on the sieve  
- \( t \) = time

This important relationship relates the probability of change to \( \sigma_{gp} \) (the log geometric standard deviation of the particle size) of the particle size distribution and to the \( \sigma_{gt} \) (the log geometric standard deviation of the time-weight curve) of the time-percent passing. It is based on the assumptions that the number of particles passing the sieve is proportional to the number that can pass the sieve at any instant, and that the passage of particles thru the sieve are independent random events. In other words, the relationship of particle size to the size of the mesh opening is of secondary importance, and that chance is the determining factor for passage of near-mesh size particles.

In summary, it becomes obvious that sieving should be continued until region 2 is reached. A good procedure might be to plot the time-weight curve on log probability paper and then
Table 2
TABLE OF SIEVES

<table>
<thead>
<tr>
<th>Country</th>
<th>Designation</th>
<th>Size Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>A.S.T.M. E-11/39 (Fine Series) Tyler N480</td>
<td>37 to 5660</td>
</tr>
<tr>
<td></td>
<td>AFNOR NF X11-501-1932</td>
<td>50 to 850</td>
</tr>
<tr>
<td></td>
<td>DIN 1171 (1934)</td>
<td>40 to 5000</td>
</tr>
<tr>
<td></td>
<td>BSS 410 (1962)</td>
<td>60 to 5000</td>
</tr>
<tr>
<td></td>
<td>Great Britain</td>
<td>76 to 3353</td>
</tr>
</tbody>
</table>

Select as an end point a time at the beginning of region 2. Sieving error may be predicted from the relationship:

$$\Delta C(W)_{t_1,t_2} = \frac{100 P_2}{\log \sigma_0} \phi(Z_m) \log \frac{t_2}{t_1}$$

(10)

where: $$\Delta C(W)_{t_1,t_2} = \text{percent passing the sieve in the time interval } t_1 \text{ to } t_2$$; $$\sigma_0$$ is the particle size distribution standard deviation; $$\phi(Z)_m$$ is the expected percent passing the sieve from the table of normal areas and ordinates; and $$P_2$$ is a constant for a given material and sieving method. $$Z_m$$ is the mean value of $$Z$$ (the number of standard deviations above or below the mean of a normal distribution) over a given time interval.

A great variety of sieves has been suggested. The common sieves used for particle size determinations are made with woven wire cloth and have square openings (Table 2). The sizes of screen openings have been standardized, and two standard series are used in the United States. These are the Tyler Standard Scale and the United States Sieve Series. Of these the Tyler series is the most useful. In it the sieve openings progress in the size ratio $$1/\sqrt[4]{2}:1$$. The designations and dimensions of the Tyler series are given in Table 3. The sieves shown in Table 3 have openings which are in the ratio $$1/\sqrt[4]{2}:1$$ with the preceding sieve openings. Every fifth sieve, therefore, will have openings in the ratio $$1/2$$.

**Sieve Frames:** Frames for all sieves of the fine series are of the standard 8-inch size, except that frames 3 inches in diameter may be used in case of sieves No. 100 and finer, used primarily in the testing of paint pigments. The standard frames are circular, 8 inches (20.32 cm) in diameter.

The height of the sieve from the top of the frame to the cloth is either about 2 inches (5 cm) or 1 inch (2.5 cm). Sieves having a height of 2 inches (5 cm) are designated as full-height sieves; those having a height of 1 inch (2.5 cm) as half-height sieves. The permissible variation on the mean inside diameter, 3/16 inch below the top of the sieve, is plus 1/32 inch. The bottom of the sieve or “sieve skirt” is constructed as to have an easy sliding fit in any sieve conforming to the above permissible variations and in no case is this outside diameter less than 7.970 inches nor more than 8.000 inches. Pans and covers are so made as to be interchangeable with standard sieves.

**Mechanical Sieve Shakers:** a) “Ro-Tap” apparatus. The “Ro-Tap” app is a mechanical shaker geared to produce 300 plus or minus 15 gyrations and 150 plus or minus 10 taps of the striker per minute; b) “End-shake” apparatus. This is a mechanical shaker with a sieve arrangement for half-height and full-height sieves. In this app, the nest of sieves reciprocates in a direction lengthwise of the gear box. The end-shake test sieving machine is a product of the Newark Wire Cloth Company of Newark, NJ.

**Dry Sieving Particle Size Determination:** The number of sieves used for a given determination depends largely upon the reason for making the determination. If a particle size distribution must be obtained, five sieves is often a satisfactory number.

The sieving operation starts by mounting the sieves in a nest, the coarsest at the top. The sample is placed on the top screen, and the screens are shaken for several minutes. It is generally impossible to screen a sample completely; the longer one shakes the screens, the more material comes thru, although to a continu-
### Table 3

Fine Series¹ — Nominal Dimensions, Permissible Variations, and Limits for Woven Wire Cloth of Standard Sieves

<table>
<thead>
<tr>
<th>Size or sieve designation</th>
<th>Sieve opening</th>
<th>Permissible variations in average opening</th>
<th>Permissible variations in maximum opening²</th>
<th>Nominal wire diameter³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2) (approximate equivalents)</td>
<td>(3) percent, plus or minus</td>
<td>(4) percent, plus</td>
</tr>
<tr>
<td>Mm</td>
<td>Inch</td>
<td></td>
<td></td>
<td>Mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(approximate equivalents)</td>
<td></td>
<td>(approximate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>equivalents)</td>
</tr>
<tr>
<td>5660 micron (No 3½)</td>
<td>5.66</td>
<td>.223</td>
<td>3</td>
<td>10.16</td>
</tr>
<tr>
<td>4760 micron (No 4)</td>
<td>4.76</td>
<td>.187</td>
<td>3</td>
<td>1.54</td>
</tr>
<tr>
<td>4000 micron (No 5)</td>
<td>4.00</td>
<td>.157</td>
<td>3</td>
<td>1.37</td>
</tr>
<tr>
<td>3360 micron (No 6)</td>
<td>3.36</td>
<td>.132</td>
<td>3</td>
<td>1.23</td>
</tr>
<tr>
<td>2830 micron (No 7)</td>
<td>2.83</td>
<td>.111</td>
<td>3</td>
<td>1.10</td>
</tr>
<tr>
<td>2380 micron (No 8)</td>
<td>2.38</td>
<td>.0937</td>
<td>3</td>
<td>1.00</td>
</tr>
<tr>
<td>2000 micron (No 10)</td>
<td>2.00</td>
<td>.0787</td>
<td>3</td>
<td>.900</td>
</tr>
<tr>
<td>1680 micron (No 12)</td>
<td>1.68</td>
<td>.0661</td>
<td>3</td>
<td>.900</td>
</tr>
<tr>
<td>1410 micron (No 14)</td>
<td>1.41</td>
<td>.0555</td>
<td>3</td>
<td>.650</td>
</tr>
<tr>
<td>1190 micron (No 16)</td>
<td>1.19</td>
<td>.0469</td>
<td>3</td>
<td>.650</td>
</tr>
<tr>
<td>1000 micron (No 18)</td>
<td>1.00</td>
<td>.0394</td>
<td>5</td>
<td>15²</td>
</tr>
<tr>
<td>840 micron (No 20)</td>
<td>0.84</td>
<td>.0331</td>
<td>5</td>
<td>15²</td>
</tr>
<tr>
<td>710 micron (No 25)</td>
<td>0.71</td>
<td>.0280</td>
<td>5</td>
<td>15²</td>
</tr>
<tr>
<td>590 micron (No 30)</td>
<td>0.59</td>
<td>.0232</td>
<td>5</td>
<td>15²</td>
</tr>
<tr>
<td>500 micron (No 35)</td>
<td>0.50</td>
<td>.0197</td>
<td>5</td>
<td>15²</td>
</tr>
<tr>
<td>420 micron (No 40)</td>
<td>0.42</td>
<td>.0165</td>
<td>5</td>
<td>25²</td>
</tr>
<tr>
<td>350 micron (No 45)</td>
<td>0.35</td>
<td>.0138</td>
<td>5</td>
<td>25²</td>
</tr>
<tr>
<td>297 micron (No 50)</td>
<td>0.297</td>
<td>.0117</td>
<td>5</td>
<td>25²</td>
</tr>
<tr>
<td>250 micron (No 60)</td>
<td>0.250</td>
<td>.0098</td>
<td>5</td>
<td>25²</td>
</tr>
<tr>
<td>210 micron (No 70)</td>
<td>0.210</td>
<td>.0083</td>
<td>5</td>
<td>25²</td>
</tr>
<tr>
<td>177 micron (No 80)</td>
<td>0.177</td>
<td>.0070</td>
<td>6</td>
<td>40²</td>
</tr>
<tr>
<td>149 micron (No 100)</td>
<td>0.149</td>
<td>.0059</td>
<td>6</td>
<td>40²</td>
</tr>
<tr>
<td>125 micron (No 120)</td>
<td>0.125</td>
<td>.0049</td>
<td>6</td>
<td>40²</td>
</tr>
<tr>
<td>105 micron (No 140)</td>
<td>0.105</td>
<td>.0041</td>
<td>6</td>
<td>40²</td>
</tr>
<tr>
<td>88 micron (No 170)</td>
<td>0.088</td>
<td>.0035</td>
<td>6</td>
<td>40²</td>
</tr>
<tr>
<td>74 micron (No 200)</td>
<td>0.074</td>
<td>.0029</td>
<td>7</td>
<td>60²</td>
</tr>
<tr>
<td>63 micron (No 230)</td>
<td>0.063</td>
<td>.0025</td>
<td>7</td>
<td>60²</td>
</tr>
<tr>
<td>53 micron (No 270)</td>
<td>0.053</td>
<td>.0021</td>
<td>7</td>
<td>60²</td>
</tr>
<tr>
<td>44 micron (No 325)</td>
<td>0.044</td>
<td>.0017</td>
<td>7</td>
<td>60²</td>
</tr>
<tr>
<td>37 micron (No 400)</td>
<td>0.037</td>
<td>.0015</td>
<td>7</td>
<td>60²</td>
</tr>
</tbody>
</table>

1 The micron designation of the fine sieve series represents a strong trend among users of precision sieves toward the use of the micron terminology in reporting particle sizes. The openings of successive sieves from the fine series progress in the ratio \( \frac{2 \sqrt[3]{3}}{1} \), and in selecting sieves from this series it is customary to take each sieve in a given range, every alternate sieve, or every fourth sieve.

2 For sieves from the 1000 micron (No 18) to the 37 micron (No 400) size inclusive, not more than 5 percent of the openings shall exceed the nominal opening by more than one-half of the permissible variation in maximum opening.

³ The average diameter of the warp and of the shaft wires, taken separately of the cloth of any sieve shall not deviate from the nominal value by more than the following:

Sieves coarser than 590 microns — 5 percent
Sieves 590 microns to 125 microns — 10 percent
Sieves finer than 125 microns — 15 percent

provided, however that for sieves finer than 125 microns, for a period not to exceed one year after the adoption of this specification, the wire diameters herefore permitted in this specification will be in effect.
ously diminishing extent. Therefore, if the results of sieve tests are to be compared, the method of shaking and the time of shaking should be standardized as in MIL-STD-1233 (Ref 21). This involves placing a 100g sample on the wire mesh of the top sieve of a nest of five sieves, shaking on a mechanical shaker for 30 minutes, and weighing the portion of the sample retained on each sieve. The sieves in the nest are of progressively finer mesh, so the weights of the portions retained on the screens constitute a set of classified particle size distribution data.

For powders which may be classified dangerous, such as finely divided Ti and Zr and mixts containing these powders, the shaking machine should be grounded and wherever possible the operation carried out behind a suitable barricade by remote control. Operators should observe all safety precautions, including the use of proper clothing, and a liq antistatic agent should be used to coat the screens and frames. A preferable alternative is to use wet sieving (see below) as well as in instances where agglomerating due to static charges may be expected.

Finally, the weight percent of the sample retained on each sieve is calcd by dividing the weight of powder on each sieve by the total weight of powder recovered. The percent of powder finer than the corresponding size of the opening on each sieve, in microns, is then plotted on log-probability paper against the size of the opening of the respective sieve, and a straight line of best fit is drawn thru the plotted points. The geometric mean, which represents the average size, is obtained by reading the 50 percent size. The standard deviation, which represents the distribution of the particles is determined by reading the 84.1 percent size and dividing this value by the 50 percent size

**Calibration of Sieves:** The US National Bureau of Standards recommends measuring the diameter of five to ten wires, making four measurements for each wire. Then the number of wires per centimeter is detd and the average size of the opening calc'd (Ref 15). Alternatively, the sieves can be sent to the National Bureau of Standards for checking. It is also ad-

### Table 4

**Variation in Results for Wet Sieve Tests**

(Tests run on a No 325 sieve at 10psi water pressure and nozzle described in ASTM Tentative Method C115-38T, and C430-75)

<table>
<thead>
<tr>
<th>Material Sample No</th>
<th>Sample, g</th>
<th>Time, min</th>
<th>Screen, inches</th>
<th>Percentage Passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica, D-2</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>78.8</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1</td>
<td>2</td>
<td>76.7</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>5</td>
<td>2</td>
<td>78.4</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>10</td>
<td>8</td>
<td>77.8</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>5</td>
<td>8</td>
<td>74.4</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>a</td>
<td>8</td>
<td>78.0</td>
</tr>
<tr>
<td>Mica, 432</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>10</td>
<td>8</td>
<td>80.7</td>
</tr>
<tr>
<td>Slate, 470</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>10</td>
<td>8</td>
<td>93.8</td>
</tr>
<tr>
<td>Coal, C</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>73.4</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>10</td>
<td>8</td>
<td>64.1</td>
</tr>
<tr>
<td>Galena, G</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>65.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>10</td>
<td>8</td>
<td>57.6</td>
</tr>
<tr>
<td>Silica, W-1</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>70.3</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>5</td>
<td>8</td>
<td>73.5</td>
</tr>
<tr>
<td>Cement, 114c</td>
<td>1.0</td>
<td>1</td>
<td>2</td>
<td>90.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

a = Wet sieving without nozzle but with light brushing
b = Standard cement sample, certified percentage passing 89.2
visable to check sieves with a standard sample to make sure that proper results are being recorded (Ref 15). Carefully sized fractions of glass beads are available from the National Bureau of Standards for calibration purposes (Ref 36).

Recent studies with different materials have shown that accurate sieve analyses of fine powders can be assured only when the sieves are pre-calibrated with samples of the particular material whose size distribution has been determined by an independent method (Refs 8 & 14).

WET SIEVING

Sievons in which a liquid is used to “wash” the material thru the screen. Wet sieving techniques are of value for such substances as the primary explosives Lead Azide and Lead Styphnate (Ref 41) which are not only hazardous in the dry state but which tend to agglomerate from the static charges generated during dry sieving. Water or an organic non-explon solvent is the preferred suspending liq. The ASTM Standard Method of Test for Fineness of Hydraulic Cement using the No 325 (45-micron) sieve is a simple, wet sieving procedure for obtaining results that can be readily duplicated. In this method a 2-inch diameter screen is sprayed with w from a nozzle at a definite pressure for a definite time (Ref 45). A comparison of some sieve data by this method for different materials is shown in Table 4.

AIR JET SCREENING

The Alpine Air Jet Sieve test equipment employs a novel vacuum sieving and mixing technique (Ref 9) which has been used to provide rapid and accurate information on the particle size distribution produced in grinding Ammonium Perchlorate (AP) used as an oxidizer raw material in solid rocket propants (Ref 17). The principles of vacuum sieving are not new. In conventional vacuum sieving, large particles tend to lodge in the sieve, blocking the sieve opening. However, the Alpine device incorporates a continuous sweeping arm with a narrow aperture along its length, on the underside of the sieve screen, thru which a jet of air passes upward thru the screen. The jet of air dislodges particles from the sieve, thus allowing effective separation as illustrated in Figure 5. The undersized particles are drawn thru the sieve by the air returning, via a suitable filter, to the suction side of a fan. The air jet method apparently overcomes several of the inherent disadvantages of conventional particle size determination. In the Tyler Ro-Tap method, clogging of the material in the sieve is experienced below 60 microns, and the particle size is determined only to approximately 44 microns. On the other hand, the Micromerograph (see below) requires tedious technician effort and lengthy test time.

Air is drawn thru the pipe to the nozzle (1); air passes thru slot in the rotating nozzle (2) to clean the wire mesh (3). The sieve chamber is sealed by a plastic lid (5). The test material is raised and fluidized in the space between the wire mesh and the lid (4). Suction is applied to pipe (6) to draw the particles thru the sieve openings.

Fig 5 Schematic Diagram of the Air Jet Sieve
Comparative tests performed on a Ro-Tap unit, a vibrating unit (Sonic Sifter — Allen-Bradley), and the Alpine Air Jet Sieve are shown in Figs 6 and 7. Fig 6 is a powdered cement; Fig 7 is cadmium stearate, a waxlike material which clogs easily. These separations were all made on a 42 micron mesh sieve. These tests showed that the Alpine Jet Sieve effected good separations in a matter of minutes compared with the much longer times required for the other systems.

The particle size distribution of AP was determined and compared using the Ro-Tap, the Alpine Air Jet Sieve and the Micromerograph. For this purpose six different samples of ground AP were chosen and separated using sieves calibrated with National Bureau of Standards spherical glass beads. The results were plotted of cumulative percent retained against the respective effective sieve openings. The average relative deviation between Ro-Tap and Alpine in the 44 to 149-micron range was found to be 4.0 percent (Fig 8). In the 25 to 75-micron range, with Alpine and Micromerograph instruments, the average relative deviation between the two methods was found to be 4.6 percent (Fig 9).

It was concluded that approximately three minutes sieving time was adequate with the air-jet sieve even with waxlike materials such as cadmium stearate; whereas, 20 minutes or longer was required for vibrating or shaking screens. The data presented (Refs 19 & 35) for AP by the Alpine, Tyler Ro-Tap, and Micromerograph agree remarkably well.

![Graph showing sieving of cement (Sieve Opening 42)](image-url)
Fig 7  Sieving of Cadmium Stearate (Sieve Opening 42)
Fig 8  Comparison of Ro-Tap and Alpine Air Jet

Fig 9  Comparison of Alpine and Micromerograph Tests
ELECTROFORMED SIEVES

The fact that the smaller woven mesh sizes are of little use for precise work has led to the introduction of the so-called micro-mesh sieves formed of nickel by a photoengraving and electroplating technique. The fragile micromesh is bonded to a supporting grid electrolytically and soldered in a 3-inch brass frame. Daeschner et al (Ref 11) first described the application of sieves in the range of 10–20 micron (Buckbee Mears Co, St Paul, Minn) to the particle size distribution of cracking catalysts. The tolerances are much finer than in conventional woven wire sieves, the aperture being guaranteed to within 2μ of the nominal size. Most of the variables associated with the use of woven-wire sieves are present in the use of micromesh sieves. Variables in the sieving procedure may be of two types: (1) those associated with the app., and (2) those pertaining to the particle

Sample Size: It is generally considered that the ideal quantity of sample is one that covers each sieve one particle deep. A more meaningful and more easily calc. estimate is the number of particles per sieve opening. Therefore, with electroformed sieves a sample not greater than 1.5g should be used. This amount corresponds roughly to 15 to 20 particles per 45μ opening and depends in practice upon the particle density and the size distribution. It is recommended that the amount of sample taken for analysis should result in a distribution of not more than 20 particles per opening for any one sieve (Ref 11).

Sievng Motion: The sieve shakers commercially available are designed to handle 8-inch sieves and, therefore, are unnecessarily bulky and powerful for a stack of 3-inch sieves. For this reason they are generally modified to permit use of 3-inch sieves by elevating the sieves and adding additional weight to the vibrating platform.

Sievng Time: Because sieving time depends upon the type of sieving motion and the provision for continuous movement of the sample over all parts of the sieving surface, the only requirement for sieving time appears to be that shaking be continued until equilibrium conditions are reached.

For some time very fine sieve plates have been made in the Netherlands (Ref 32). Unlike the American micro-mesh sieve gauze, the openings of this plate are round and conical, as a result of which the open area percentage is smaller than of the micro-mesh gauze (Table 5).

<table>
<thead>
<tr>
<th>Nominal Opening in microns</th>
<th>Open Surface Area, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-mesh, square</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>3.5</td>
</tr>
<tr>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>45</td>
<td>28</td>
</tr>
<tr>
<td>90</td>
<td>44</td>
</tr>
<tr>
<td>Microplate, # round</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2.5</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
</tr>
</tbody>
</table>

* American Manufacture
# Dutch Manufacture

An advantage of this, however, is that the sieve plate is more robust and less liable to be damaged. Owing to the conical shape of the openings, the danger of clogging is at a minimum (provided the sieve is used in the right direction). Figure 10 shows a cross-sectional drawing of this Dutch micro-mesh sieve plate.

For substances with particles of 20 microns and coarser, sieving with these sieves is possible in many cases by the normal dry methods. To obtain optimum results, however, it is advisable to use a liq. With sieves of 15 microns and finer,
dry sieving is very difficult or even impracticable. The following is the procedure recommended by The Central Technical Institute of the Netherlands (Ref 32): The sieve is dried at 70° to constant weight. After cooling in a desiccator, about one gram of the sample is put on the sieve and weighed accurately to ± 0.2 mg. Next, the sieve is very carefully immersed and supported in a beaker of non-solvent, low-viscosity liq. The sieve is then raised and lowered so that the liq flows back and forth thru the openings and the fine particles pass thru. By generating ultrasonic vibrations of 40 kc/sec in the bath with a suitable generator, the sieve openings can be prevented from clogging. The liq in the bath is repeatedly replaced at five minute intervals until no further passage of particles can be visually observed. Next, the micro-mesh sieve is dried at 70° together with the retained sample and, after cooling, weighed on an analytical balance, and the percentage retained for the relative sieve opening determined.

Micro-mesh sieves have been applied to the determination of solid proplnt ingredients (Refs 17 & 35) and similar materials where sieve analyses are required with great accuracy in the very fine range. They are also applicable to specific problems such as the analysis of magnetic powders, and of powders consisting of mixts of substances of different specific gravities or the preparation of clearly defined particulate fractions in a short time. The particle-size distribution of two test powders, spherical glass beads and crushed quartz was determined with different types of app (Ref 32), and indicate that the micro-mesh sieve data is in good agreement with those of other methods (Table 6):

<table>
<thead>
<tr>
<th>Particle limit in microns</th>
<th>Sedi-ment-meter</th>
<th>Sediment balance</th>
<th>Pipette (Andreasen)</th>
<th>Micro-mesh sieves</th>
<th>Coulter Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample: quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>91</td>
<td>89.5</td>
<td>94</td>
<td>91.5</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>86</td>
<td>91.5</td>
<td>87</td>
<td>91.5</td>
</tr>
<tr>
<td>4</td>
<td>81</td>
<td>83</td>
<td>88</td>
<td>82</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>74</td>
<td>78</td>
<td>81.5</td>
<td>74.5</td>
<td>81.5</td>
</tr>
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<td>76</td>
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<td>60</td>
<td>70</td>
<td>71.5</td>
<td>65</td>
<td>71.5</td>
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<tr>
<td>15</td>
<td>46</td>
<td>58.5</td>
<td>61</td>
<td>52.5</td>
<td>64.5</td>
</tr>
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<td>40</td>
</tr>
<tr>
<td>40</td>
<td>—</td>
<td>19</td>
<td>10</td>
<td>15</td>
<td>28.5</td>
</tr>
<tr>
<td>Sample: Spherical glass beads</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>97.5</td>
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<td>98</td>
<td>—</td>
<td>98.5</td>
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<td>96</td>
<td>95</td>
<td>95.5</td>
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<td>90.5</td>
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<td>82.5</td>
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<td>87</td>
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<td>48.5</td>
<td>42.5</td>
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</tr>
<tr>
<td>40</td>
<td>—</td>
<td>28</td>
<td>36</td>
<td>—</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 6
Comparison of Particle-Size Analyses by Various Methods
Percentage greater than limit determined with:
Irani and Callis (Ref 14) used two parameters of the distribution of ground monocalcium phosphate (which follows the commonly used log normal distribution law): namely, $M_g$ and $\sigma_g$, the geometric mean diameter and the geometric standard deviation, to evaluate the precision and accuracy of electro-formed sieves vs sedimentation as a reference procedure:

**Two samples in two size ranges by two operators:**

<table>
<thead>
<tr>
<th>Confidence</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_g$</td>
<td>$\sigma_g$</td>
</tr>
<tr>
<td>Replicated five times—Sieves</td>
<td>$\pm 2.6%$</td>
</tr>
<tr>
<td>Replicated seven times—Sedimentation</td>
<td>$\pm 7.8%$</td>
</tr>
</tbody>
</table>

Although the screens are more precise than sedimentation, they could not be more accurate because they were calibrated from the sedimentation values.

**Eleven samples not used for calibration of sieves:**

<table>
<thead>
<tr>
<th>Confidence</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_g$</td>
<td>$\sigma_g$</td>
</tr>
<tr>
<td>Geometric mean diameter and standard deviation between electro-formed sieves &amp; sedimentation</td>
<td>$\pm 4.7%$</td>
</tr>
</tbody>
</table>

The foregoing close agreement of the geometric mean diameter and geometric standard deviation results indicates that accuracy evaluations were made on an absolute scale, and did not refer to some arbitrary scale.

To evaluate the effect of shape factors of particles, the electro-formed sieves were calibrated microscopically with two different materials:

**Table 7**

<table>
<thead>
<tr>
<th>Calibration of Sieve Openings — Microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve</td>
</tr>
<tr>
<td>Microscope</td>
</tr>
<tr>
<td>Ground</td>
</tr>
<tr>
<td>Monocalcium Phosphate</td>
</tr>
<tr>
<td>Spherical</td>
</tr>
<tr>
<td>Glass</td>
</tr>
<tr>
<td>Beads</td>
</tr>
</tbody>
</table>

It is evident from the above that micromesh sieves must be calibrated for every material and sieving method for which they will be utilized. When properly calibrated, precision, electro-formed micromesh sieves are useful as reliable primary standards for determining particle size distributions of energetic materials. They are characterized by the following significant features: 1) the uniformity of the openings is such that a precision of 1 to 2 per cent is easily attainable; the accuracy for spheroidal particles, is equal to that by microscopic measurements; 2) the micromesh openings may be reliably measured with a microscope; 3) because of the physical size of the sieves, the sieving rate may be precisely and conveniently followed with an analytical balance and the degree of blinding and agglomeration followed with an ordinary microscope; and 4) compared to the use of woven-wire sieves, the micromesh sieves require less sample and less sieving time, and, because of the uniformity of openings which are in a single plane, the micromesh sieves blind less and give a more accurate separation according to particle diameters.

**ELUTRIATION PROCESSES**

(Fluid Moving)

Elutriation differs from sedimentation in that fluid moves vertically upwards and thereby carries with it all particles whose settling velocity by gravity is less than the fluid velocity. In practice, complications are introduced by such factors as the non-uniformity of the fluid velocity across a section of an elutriating tube, the influence of the walls of the tube, and the effect of eddies in the flow. In consequence, any assumption that the separated particle size corresponds to the mean velocity of fluid flow is only approximately true; it also requires an infinite time to effect complete separation. This method is predicated on the assumption that Stokes’ law relating the free-falling velocity of a spherical particle to its density and diameter, and to the density and viscosity of the medium is valid.

In this method, the free-falling velocity of particles of selected size, in still air, is counter-balanced by an upward, uniform flow of air or gas at the same (free-falling) velocity. Particles
smaller than the selected size will be carried away and collected, while larger particles will fall. This method is not suitable for fractionation in the 0 to 5 μ range and is, therefore, recommended for those powders whose particle size distribution is such that knowledge of the amount contained in the 0 to 5 μ range (as well as amounts in the coarser ranges) will suffice. The method is strictly accurate for solid, spherical particles of a limited size range and becomes progressively less accurate with increasing particle diameter, with increasing departure from the spherical shape, or with increasing porosity.

The rate of air flow may be determined directly from charts supplied by the manufacturers or calculated from Stokes' equation as follows:

\[ V = 10^{-8} \frac{g}{P} \left( \frac{D^2}{18N} \right) \]  \tag{11}

where:  
\( V \) = velocity of a falling spherical particle in still air or gas, cm/s  
\( g \) = gravitational constant, 980 cm/s²  
\( P \) = absolute density of particle, g/cm³  
\( N \) = viscosity of air or other gas  
\( d \) = diameter of particle, μ

Thus, at 20°C, for air:

\[ V = 29.91 \times 10^{-8} \times P D^2 \]  \tag{12}

The volume rate of air flow, \( F \), in cubic centimeters per minute required to balance the settling velocity of the largest particle which it is desired to float is given by the following equation:

\[ F = 47.1 \times V \times D^2 \]  \tag{13}

where:  
\( V \) = free falling velocity, cm/s  
\( D \) = diameter of the settling chamber, cm

Gravitational Methods

GONELL AIR ELUTRIATOR. This is the prototype of all analytical separators with laminar air flow. It consists of a cylindrical brass tube (or a series of tubes) with a conical base. An air inlet is provided in this base on the axis of the tube. The sample of powder is placed in the inlet cone, and air is blown thru the largest tube until separation is deemed complete, or for specified periods of time. The residue is removed, weighed, and transferred to a smaller diameter tube, and the test is repeated. The tube should have polished internal surfaces and should be periodically tapped or vibrated to disturb settled powder.

Batel (Ref 9) pointed out that because the air flow thru the elutriator is streamline, the velocity gradient across the tube diameter is para-

bolic. The max velocity at the center of the tube is twice the average velocity. It is expected that this velocity distribution has a similar effect upon the analytical results that variations in screen has upon screening analyses, and sharp separations are not possible. He also found that particle sizes in the separation process depend upon the duration of elutriation as shown in Fig. 11:

![Figure 11](image)

Fig 11 Effect of elutriation time on the amount of residue in the glass attachment of the Gonell Separator for different tubes and air mounts

From several values given above, the characteristic granularity curves were set up as function of the elutriation time:

![Figure 12](image)

Fig 12 Relation of the granularity characteristic curves to the elutriation times at 5.5 hours and at 1.5 hours in the Gonell Separator
Fig 13  Air Classifier for Subsieve Particle Size Analysis
ROLLER AIR ELUTRIATOR. The app consists essentially of a series of vertical settling chambers of different diameters (in the ratio of 1:2:4:8) in which the uniform upward flow of air is maintained (Ref 42). These are interchangeably connected as shown in Figure 13, at the lower end to a blowing tube (U-tube), in which the sample is dispersed, and at the upper end to a collection system which is usually an Alundum extraction thimble. The app is arranged to provide for the direct impingement of a high-velocity air or gas jet against the powder sample and for the recirculation of the uncollected fraction. Duchesne and Reite (Ref 35) evaluated this instrument for the analysis of castable rocket propalns. Optimization of particle size distributions was the first objective, with high solids processing and the availability of reliable methods for the determination of this parameter being important. The Alpine Air Jet Siever had been used for those powders coarser than 32 microns; however, the finer particles of Al and of AP were of considerable concern. Even though the Micromerograph failed to sediment the entire sample of castable rocket propalns it was commonly accepted as the principal app for fine powder analysis. For these reasons the Micromerograph was experimentally compared to the Mine Safety Appliances app (M.S.A.), Whitby Liquid Sedimentation app (Ref 12) and to the Roller Air Analyzer (Ref 42). Results are summarized in Fig 14 for Al powder. Consider-

---

![Graph](image)

**Fig 14** Comparison Between Three Test Methods for Particle Size Distribution of H-15 Al Powder
ing the major differences in techniques, the bias between the three methods was quite acceptable. Earlier, Eigsti and Dwiggins (Ref 16) had found the Roller instrument unsuitable for the particle size determination of chemical delay compons used in solid rocket propellant systems, because once the sample was separated into fractions by the elutriator, each fraction would need to be analyzed by some other method to determine its actual size distribution. Also, if 10% or more of the particles were less than $5 \mu$ in diameter, a complete fractionation would require about 8 hours, considered to be a prohibitively long time.

**Centrifugal Methods**

Efforts to overcome the problems of long elutriation times of the gravitational separators led to the development of centrifugal separators, since the falling speed of the particles can be increased by using centrifugal fields. Then the law of resistance for the laminar free-falling velocity is replaced by that for the turbulent free-falling velocity. This fact, as well as the difficulty of allowing for the velocity field of the air, precludes a calen of the particle size for analytical purposes. These analytical separators are, therefore, calibrated with spherical granules. Since the resistance in turbulent air currents also depends upon the particle shape, this calibration is only conditionally valid for technical powders in which particle shapes deviate more or less from the spherical shape.

**BAHCO CENTRIFUGAL CLASSIFIER.** This is a proprietary instrument that is essentially a centrifugal air elutriator. Air and dispersed powder samples are drawn thru the cavity of a rotating hollow disc in a radially inward direction against centrifugal forces. The powder particles are thus divided into under- and oversize fractions, collected, and weighed. Separation into different size-fractions is made by altering the air velocity. About 20g of sample are required for analysis, and 8 size determinations can be made in 2 hours (Ref 10).

Batel (Ref 9) made a comparison of separation and sedimentation results as shown in Figure 15. The results of separation by Bahco, Gonell, and Air Jet tie in very well with the results of sedimentation (Andreasen and Sartorius).

**SEDIMENTATION PROCESSES**

(Fluid Static)

Sedimentation processes are those in which the rate of settlement of particles in a static fluid is measured, the analysis being either with the particles uniformly dispersed throughout.

![Granularity characteristic curves of an identical quartz dust obtained by different analysis methods](image)
the whole of the fluid, or introduced at the top of a column. The rate of sedimentation usually follows Stokes’ law, and settlement may be under conditions of gravitational acceleration, or under centrifugal acceleration, imposed by rotation of the entire system, in order to increase the rate of sedimentation. Stokes’ law is valid only in the regime of viscous flow, which sets an upper limit to the size of particle that can be tested by this means in a given fluid. The limit is determined by the magnitude of the Reynolds number, which should not exceed 0.2 if the error when Stokes’ law is used is not to exceed 5 percent. The concn of the suspension should always be as low as possible in order to avoid interference between particles, particularly since “clouds” of particles tend to move en masse and not individually. The method of measurement, eg, by weighing, may dictate a lower limit of concn beyond which inaccuracies become unacceptably high.

Effective dispersion of the particles is an essential prerequisite for all methods of sedimentation analysis. It is often necessary not only to stir the suspension vigorously prior to analysis, but to introduce the powder already mixed with a dispersing agent. A further agent to prevent flocculation may be needed, and it may be necessary to adjust the pH of the suspension to a suitable value determined by experiment.

**Sedimentation Columns: Liquid**

A suspension uniformly dispersed in an upright cylindrical vessel at time $t = 0$ begins to settle immediately. If two horizontal planes, $p_1$ and $p_2$, are taken at depths $h_1$ and $h_2$ below the upper surface ($h_1 > h_2$), then, at time $t$, the mass of suspension remaining between $p_1$ and $p_2$ will be determined by $(h_1 - h_2)^3$, plus particles that have fallen thru $p_2$ minus particles that have fallen thru $p_1$, where $\sigma = $ mass per unit depth of original suspension.

For incremental methods of analysis, the sample is theoretically taken from an extremely thin layer in which $h_2$ is nearly equal to $h_1$; for cumulative methods of analysis, the amount settling in a particular plane in a given time, normally at the bottom of the settling vessel, is measured.

**MSA-WHITBY PARTICLE SIZE ANALYZER.**

The main features of this method are that it uses gravitational settlement followed by centrifugal sedimentation. A thin layer of the sample suspension is superimposed on a column of clear liq so that all particles begin to settle from the same level. The initial suspending medium is chosen to have a density slightly less than that of the sedimentation liq. The amount of solid sample required for the analysis is a few milligrams.

The app consists of a glass centrifuge tube, 14mm internal diameter, ending at the bottom in a graduated capillary tube, 1 mm internal diameter as shown in Fig 16. A feed- or sample introduction-tube is provided. This is a short metal tube that fits easily into the mouth of the glass centrifuge tube.

In operation, the centrifuge tube is filled with the sedimentation liq to within 10mm of the top. The feed-tube is then filled with the sample suspension and the upper end is closed by the operator’s finger. The feed-tube is then placed in the centrifuge tube with the suspension in contact with the column of clear sedimentation liq; this starts the sedimentation. The finger is then removed.

Gravitational settlement is allowed to proceed for 4 to 10 minutes, according to the particle-size range of the sample. The sedimentation tube is then centrifuged to reduce the time required for the smaller particles to reach the bottom. By measuring the volume of particles accumulated as a function of time, the equivalent spherical size distribution of the sample may be computed from formulae based upon Stokes’ law. In addition to the specially designed sedi-

![Fig 16 Sedimentation Tube and Sample Introduction Chamber](image-url)

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*P38*
mentation tubes, the major items of app include two to four constant speed centrifuges (300 rpm to 3600 rpm) driven by hysteresis-type synchronous motors, having stable starting and stopping characteristics, including a max rate of acceleration of five radians per second and the ability to be stopped and started by an interval timer.

The principal steps in this method are as follows: 1) select sedimentation and dispersion lig and determine density of the sample; 2) calculate a particle size-settling time table for gravity settling and for various centrifuge speeds; 3) disperse the sample in dispersing lig; 4) prepare the sedimentation tube and initiate the run by introducing the sample dispersion; 5) record the readings of the sediment height (to the nearest 0.1mm) in the capillary of the sedimentation tube at the times previously calculated for the various particle sizes; and 6) calculate and plot the cumulative size distribution curve from the size-time table.

Procedure: (1) In selecting the sedimentation and dispersing lig to be used, several factors need to be considered. Obviously, the lig must be inert to the material to be examined and must be miscible with each other. Both must also adequately disperse the sample during sedimentation or suitable surface-active agents must be added. For convenience, the viscosity and density of the sedimentation lig should be such that the largest particles present do not settle out sooner than 10 sec after the start of the run, since it is difficult to obtain the first reading before this time

(2) The time required for a spherical particle to settle under gravity to the bottom of the tube is derived from Stokes' law:

\[ t = \frac{18 \times 10^8 \eta h}{(P_1 - P_0) g d^2} \]  

where:
- \( \eta \) = viscosity of the sedimentation liquid, poise
- \( h \) = total settling depth, cm
- \( P_1 \) = skeletal density of sample, g/cm³
- \( P_0 \) = density of sedimentation liquid, g/cm³
- \( g \) = gravitational acceleration constant, cm/sec²
- \( d \) = Stokes equivalent particle diameter, \( \mu \)

During the gravity settling period sample particles become classified, all particles larger than or equal to a certain diameter, \( \sigma \), will have settled to the bottom of the centrifuge tube, while all particles smaller than this diameter will have settled a lesser distance. If the succeeding settling under centrifuging took place at constant speed, the derivation of a table of desired centrifuge times corresponding to various diameter particles would be straightforward. However, the centrifuge is actually started and stopped between readings so that a small correction, \( \alpha \), must be determined and added for each speed and centrifuge. Cartwright and Gregg (Ref 12) in their investigation of the particle size distribution of Ammonium Nitrate described a procedure for calculating \( \alpha \) and incorporating it in the derived formula for centrifuge settling time:

\[ t' = \frac{18 \times 10^8 \eta}{(P_1 - P_0) w^2 d^2} \ln \left( \frac{r_2}{r_0 + d^2 h/\eta^2} \right) + \alpha \]  

where:
- \( t' \) = Centrifuge settling time
- \( w \) = angular velocity of centrifuge, radians/sec
- \( r_0 \) = distance from rotation axis to surface of sedimentation liquid in tube, cm
- \( r_2 \) = total distance from rotation axis a particle settles = \( r_0 + h \), cm
- \( \sigma \) = diameter of last particle just sedimented during gravity settling portion of run, \( \mu \)
- \( \alpha' \) = centrifuge start-stop correction, sec

As mentioned, the data obtained by this method are expressed as cumulative size distribution curves. Since the computations assume Stokes' law for spherical particles, the plotted curves give the distribution of spherical particles which would behave like the actual sample with respect to this experiment. For this reason, the sizes on the distribution curves should be labelled "Stokes Equivalent Diameter". Because of the underlying assumptions and the above interpretation of the results, it is clear that the repeatability of this method has more meaning than accuracy of comparison with results of other methods.

Data given in Table 8 and Fig 17 for a ground Ammonium Nitrate illustrate the degree of re-
Fig 17 Sedimentation Analysis of Ammonium Nitrate

Peatatability possible with this technique. The max deviation from the individual mean is 1.2 weight percent and the average deviation is 0.5 weight percent.

For the particle size measurements of boron and barium dichromate, components of pyrotechnic delay compns, Freeman (Ref 46) evaluated the M.S.A. Particle Size Analyzer versus microscopy, gravitational liq sedimentation, electrostatic resistivity change, and permeability to fluid flow technique. The conclusion was that the M.S.A. Analyzer was the only available app suitable for the analysis of particle size distribution of substances containing particles as small as 0.1 micron. In initiating the analysis of new materials by this method it was found that evaluation of dispersing agents and methods was the most time-consuming phase.

Table 8
M.S.A.-Whitby Particle Size Analyzer
Data for Ammonium Nitrate

<table>
<thead>
<tr>
<th>Stokes’ Equivalent Diameter, μ</th>
<th>Sediment Height, mm</th>
<th>Weight Finer than Size, percent</th>
</tr>
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<tr>
<td>70</td>
<td>0.02</td>
<td>99.8</td>
</tr>
<tr>
<td>60</td>
<td>0.1</td>
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<td>88.3</td>
</tr>
<tr>
<td>40</td>
<td>2.6</td>
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<td>35</td>
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<td>62.4</td>
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<td>30</td>
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</tr>
<tr>
<td>8</td>
<td>9.3</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>9.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>
The selection of an optimum surfactant, or combination of surfactants, was necessary primarily to prevent re-agglomeration of the dispersed sample while settling. In addition, it was demonstrated that the use of a blender (Waring) was an effective aid in dispersing these two components. The violent action of the blender did not cause a change in the concen of coarse particles in the dispersion with increasing blending times up to 17 minutes.

Alley and Dykes (Ref 39), as well as Abbot et al (Ref 37), conducted studies of the M.S.A. method, especially suitability of the method for use as a standard specification procedure for the oxidizer used in double-base propellants, based on an estimate of its precision. Single analyses of two different Ammonium Perchlorate samples, having weight median diameters in the range of 20-30 microns, were made by each of nine laboratories thru use of the same liq sedimentation technique and calibrated equipment. The precision of analyses was considered to be adequate, and the fact that a number of laboratories are successfully using the procedure supports this conclusion. However, the method was not recommended as a standard specification procedure for the particle size analysis of nominal 20- to 30-micron Ammonium Perchlorate, because of the large systematic error among laboratories in the determination of specific surface area. This could be due to some deficiency in the analytical procedure that permits the introduction of variations by the laboratory personnel. One likely source of inconsistency is in the dispersion of the Ammonium Perchlorate particles. The accuracy of the method was not estimated in this study because a standard Ammonium Perchlorate sample of accurately known particle size was not available. A highly significant correlation was found between the average particle diameter (APD) determined with the Fisher Sub-Sieve Sizer and the mean of the particle diameters derived from the log-normal distributions of 33 samples of Ammonium Perchlorate determined by M.S.A. analysis (Ref 37). Generally the APD is smaller than the mean particle diameter. This is to be expected since the principles on which the Fisher Sub-Sieve Sizer is based results in a “surface” average rather than the “weight (volume)” average on which the M.S.A. measurement is based.

Sedimentation Columns: Gas
SHARPLES MICROMEROGRAPH. A commercially available air sedimentation device introduced in 1953 (Ref 6) that provides rapid particle size distribution determinations for powdered materials by the application of Stokes' law for particles falling thru a static column of gas.

As described by Kaye et al (Ref 22), the powder sample is injected downward into the top of the settling column thru a powder feed system and deagglomerator. A small pressure chamber, connected to the powder sample chamber by a solenoid valve, is charged with dry nitrogen to a predetermined pressure. When the solenoid valve is actuated, the nitrogen discharges thru the powder sample chamber and carries the powder at high velocity thru a narrow conical slit in the deagglomerator. The powder is dispersed by the aerodynamic shear forces in the deagglomerator slit. These forces can be varied within wide limits by the choice of pressure in the pressure chamber, and by the choice of the deagglomerator slit width. The pressure is variable from 0 to 400 psi, and the slit width may be adjusted from 10 to 250 microns.

The sample then enters the vertical, approximately seven-foot long, insulated aluminum, settling column where the particles reach terminal velocities, and fall until stopped by the pan of the servo-electronic balance at the bottom of the column. As the particles accumulate on the balance pan, a slight rotation of the balance beam on its torsion suspension occurs. A sensing device incorporated in the balance applies a current to a restoring force coil on the balance beam. The current required to balance the accumulating weight of the powder on the balance pan actuates the milliammeter of a moving chart recorder. This accumulated weight-time curve is interpreted by using two templates which are based on experimental calcns and are reported to take into account discrepancies arising due to nonsphericity of the particles and variations in initial velocity.

The performance of the Micromerograph has been of interest ever since its introduction because of its potential for a much needed improvement in the analyses of the important sub-sieve sized ingredients of Ordnance. It has been evaluated relative to several other instruments: Coulter Counter.
(Refs 16, 28, 29 & 31); Microscope (Refs 20 & 27); Fisher Sub-Sieve Sizer (Refs 16 & 27); Cenco Photometer (Refs 16 & 28); MSA-Whitby (Ref 25); Cintel Flying Spot Counter (Ref 20); Ro-Tap Siever (Ref 18); and Andreasen Pipette (Ref 31).

The advantages most frequently observed were:
1. Simplicity and ease of operation. (Refs 20 & 25)
2. Economy of operator time. (Refs 19 & 22)
3. Reproducibility (especially within a single instrument) (Refs 18 & 19)

The disadvantages observed were:
1. Low recovery of charged sample. (Refs 16 & 31)
2. Electrostatic charge on particles. (Ref 16)
3. Variations between instruments. (Refs 16a & 29c)
4. Lack of accuracy. (Ref 22)

Probably the most common criticism of the Micromerograph was that of low recovery of the material charged which generally ranged from only 30–50%. The low recovery is in part due to

<table>
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<tr>
<th>Laboratory</th>
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<th>Ave (X)</th>
<th>Range (R)</th>
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<th>22.1</th>
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<th>4.9</th>
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<td></td>
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<td>5.5</td>
<td>4.2</td>
<td>1.4</td>
<td>137</td>
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</table>
electrostatic charge induced on the particles causing them to be attracted to the walls of the column (Refs 16 & 22)

Long (Ref 16a) has reported on an evaluation of the reproducibility of the instrument conducted by nine laboratories using twelve different instruments to analyze portions of the same ground silica (Table 9). An analysis of variance showed inconsistency among the laboratories and between instruments within the laboratories; this reflected inconsistency among instruments regardless of their location. The testing errors between runs from the same instrument in the same laboratory were, for the most part, fairly comparable. It was concluded that although individual instruments gave reproducible results, a comparison between laboratories of particle size for a given material could not be easily accomplished.

Despite shortcomings, the Micrometerograph in the early 1960's was the only instrument generally available for determining particle size distribution of sub-sieve proplnt and pyrotechnic ingredients. In general, it appears that the Micrometerograph, provided that frequent calibration checks are performed, is a good, reproducible instrument for size measurement. The operator time involved is less than with most other methods, and the calçens are not complicated. As in all sedimentation methods, only when the sample particles are spherical does the "Stokes' diameter" that is measured become a measure of absolute particle size. Microscopic examination should be used to check on particle shape and the effect of de-agglomeration.

**Pipette Methods**

In this technique, a sample is extracted from the sedimenting suspension at appropriate intervals by means of a pipette. These methods are incremental, and the sample is taken in one of two ways: (a) at a fixed position in the app, or (b) at a fixed depth below the surface of the suspension. It is assumed in both instances that no disturbance of the suspension takes place by eddies, etc., while the sample is being taken, that the sample is representative of the suspension at the extraction point, and that the sample taken is small. Method (a) must take into account any lowering of the level of the top surface of the suspension.

**ANDREASEN PIPETTE.** This is probably the most frequently used method of sedimentation analysis, the disadvantage being that samples withdrawn must be evaporated to dryness and weighed — a time-consuming procedure (Ref 31).

The glass sedimentation vessel is about 5.5 cm in diameter and has a graduated scale, 0 to 20 cm, engraved on its side. The zero of the scale is positioned about 2.5 cm from the base of the vessel, and the capacity when filled to the 20 cm mark is 550 to 600 ml. The stem of the pipette is fused to a bell-shaped bulb having a ground-glass joint that fits the neck of the sedimentation vessel, the pipette being so positioned that its tip is fixed at the level of the zero mark of the scale; above the bulb is a two-way tap and a side discharge tube. During an analysis, the sedimentation vessel is immersed in a constant-temperature bath up to the 20 cm mark.

The vessel is filled with suspending liquid and the powder to be analyzed to the 20 cm mark, shaken to disperse the sample, and placed upright in the bath. At time intervals, standing in a 2 to 1 progression, a 10 ml sample is withdrawn from the sedimentation vessel and is discharged into a series of tared dishes. The dishes are reweighed after the samples have been evaporated to dryness, and a deduction is made for the weight of any dispersing agent added; thus, the weight of particles corresponding to each withdrawal time is determined.

The size of particles is calculated from the height of fall and time elapsed, according to Stokes' law, but allowance must be made for the decrease in height of sedimentation column after each sample is withdrawn. The initial concn in the suspension is calculated from the weight of powder and the volume of liq in which it has been dispersed. This concn may be up to one percent by volume for easily dispersed powders, but should be reduced if there is any tendency for flocculation to occur. This app is normally applicable to the particle size range 2 to 60 μ, and may be extended to larger sizes if viscous liquids are used, eg, benzyl alc, or to smaller sizes if constant temp is maintained over the longer period required. One operator can perform four analyses simultaneously during a day. The weight of powder required is approximately 5 g.

**Density Variation: Gravimetric HYDROMETER METHOD.** The suspension of a powder is prep'd as for other sedimentation
analyses and poured into a 1, glass measuring cylinder. The variation with time of effective density, and hence of particle concn., is determined from readings of a hydrometer immersed in the suspension. The hydrometer should be inserted in the suspension immediately before the reading is taken, and afterwards removed to avoid particle deposit on the bulb. The effective height of the suspension is from the surface level to the center of volume of the bulb, which varies according to the density of the suspension. As the bulb length is an appreciable proportion of the sedimentation height, and not very small, the incremental method of calculating the size analysis is only approximate. Temp and meniscus corrections should be applied. Eigsti and Dwiggins (Ref 16) evaluated this method for particle size measurement of chemical delay compns but found it unsuitable because of the disadvantages mentioned above.

**DIVER METHOD.** This is a modification of the hydrometer method. Variation in effective density, and hence concn., is measured by totally immersed divers. These are small glass vessels of approximately streamline shape, ballasted to be in stable equilibrium, with the axis vertical, and to have a known density slightly greater than that of the sedimentation liq. As the particles settle, the diver moves downwards in hydrodynamic equilibrium at the appropriate density level. The diver indicates the position of a weight concn equal to the density difference between the diver and the sedimentation liq. Several divers of various densities are required, since each gives only one point on the size distribution curve.

The advantages claimed for this method over the hydrometer method are that, since the divers are relatively small and surface tension and deposition effects are avoided, the incremental theory is applicable. Smaller divers can be used with centrifuge tubes, so that analysis can be extended down to particles of 0.02 µ in size. Eigsti and Dwiggins (Ref 16) pointed out the disadvantages were that a large concn is necessary, thus particle interference and agglomerations may be present. Since the divers are placed directly in the suspension, they may interfere with the settling process. For these reasons and the length of time involved in obtaining the necessary data this method is considered to be generally undesirable for either control or laboratory determinations of chemical delay compns.

**Density Variation: Absortiometric**

Turbidimetric methods for particle size analysis (Refs 10, 16 & 27) are used in conjunction with sedimentation procedures to determine the concn of particles at given distances below the surface at successive time intervals. From these data, and Stokes' law, particle size distribution can be calculated.

When a beam of light is intercepted by a turbid medium, part of the incident light is absorbed, part is directly reflected, and part is scattered. The attenuation produced is a function of the concn, particle size distribution and color of the suspension.

If light attenuation is due mainly to scattering, which is usually the case in turbidimetry, the usual light transmission equation may be written:

\[
\frac{I}{I_0} = e^{-(K\pi r^2 nl)}
\]

where:  
- \(I\) = Intensity of light transmitted  
- \(I_0\) = Intensity of incident light  
- \(K\) = total scattering coefficient = the effective scattering cross section divided by the geometric cross section  
- \(\pi r^2\) = cross sectional area of particle  
- \(n\) = number of particles per unit volume of dispersion  
- \(l\) = length of light path thru suspension

Values of \(K\) have been tabulated for particles of various diameters. For extremely small particles \(K\) is nearly zero. Its value increases rapidly to between 3 and 5 for particles in the range of approx 0.3 to 0.7 microns. As the size of the particle increases, \(K\) drops to a constant value of 2. When values of \(K\) are known, and when either the particle diameter or the number of particles is known, the other may be determined from the ratio \(I/\)\(I_0\). If both \(n\) and \(r\) are unknown, they may be determined by making transmission measurements at two different wavelengths and setting up simultaneous equations using equation (16)
Thru a combination of sedimentation and transmission measurements, a particle size distribution can be found. Tranquil settling of a dispersion of non-uniform particles will result in a separation of particles according to size so that transmission measurements at known distances below the surface at selected time intervals, will, with Stokes’ law, give the conc of particles of known diameter. Thus, a size frequency distribution can be obtained

**EAGLE-PICHER TURBIDIMETER.** Based on the research of Harner and Musgrave (Ref 10) is an app which comprises a stable light source, a sedimentation cell, and a photocell and microammeter as illustrated in Fig 19:

![Diagram of Apparatus Showing the Important Elements of its Construction](image)

Fig 19 Schematic Diagram of Apparatus Showing the Important Elements of its Construction

1. 6-v spotlight bulb
2. Parabolic reflector
3. Condensing lens system
4. Heat filter glass
5. Adjustable iris diaphragm
6. Cell housing
7. Cell level adjustment
8. Sedimentation cell
9. Light slot
10. Secondary condensing lens system
11. Barrier-layer type photocell
12. Microammeter

The light beam traverses the suspension at a fixed distance below the surface. A plot is made of the percent light attenuated versus time from the microammeter readings. From this, increments of light attenuation for various size ranges are determined. These values are converted to weight percent by the use of “equivalent hiding power” factors.

The usual problems encountered with any sedimentation procedure are present. It is necessary to use a dispersing liq compatible with the material being tested. Also, dispersing agents and technique must insure complete dispersion and prevent agglomeration. These factors may vary with materials, and therefore will require special attention when new materials are to be analyzed.

In connection with the burning time of chemical delay compns Eigsti and Dwigglins (Ref 16)

<table>
<thead>
<tr>
<th>Sample Lots</th>
<th>Turbimeter Wgt. Ave. Diameter (μ)</th>
<th>Specific Surface (cm²/gm)</th>
<th>Micromerograph Wgt. Ave. Diameter (μ)</th>
<th>Specific Surface (cm²/gm)</th>
<th>Coulter Counter Wgt. Ave. Diameter (μ)</th>
<th>Specific Surface (cm²/gm)</th>
<th>Specific Surface (cm²/gm)</th>
<th>B.E.T.</th>
<th>Burning Time (sec/in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-10*</td>
<td>1.5</td>
<td>1795</td>
<td>2.3</td>
<td>1377</td>
<td>11.8</td>
<td>781</td>
<td>1000</td>
<td>3.41</td>
<td></td>
</tr>
<tr>
<td>M-20*</td>
<td>3.1</td>
<td>1107</td>
<td>2.5</td>
<td>1227</td>
<td>11.5</td>
<td>817</td>
<td>1000</td>
<td>4.62</td>
<td></td>
</tr>
<tr>
<td>ND 3499**</td>
<td>5.4</td>
<td>688</td>
<td>4.9</td>
<td>709</td>
<td></td>
<td></td>
<td></td>
<td>42.04</td>
<td></td>
</tr>
<tr>
<td>ND 3657**</td>
<td>6.5</td>
<td>553</td>
<td>5.0</td>
<td>674</td>
<td></td>
<td></td>
<td></td>
<td>44.96</td>
<td></td>
</tr>
</tbody>
</table>

* Samples obtained from Sylvania Electric Products, Inc
** Samples obtained from Fansteel Corp

**Table 10:** Comparison of Results From Four Particle Size Methods
Since the foregoing tests were carried out at identical conditions of compn and temp, and in a standard test fixture, the burning times serve as a means of checking the relative fineness of the powdered tungsten fuels. The rapid burning times indicate that both M-10 and M-20 are very fine. Also, the M-10 is definitely finer than M-20, as shown by the difference in burning times.

The specific surface being a gauge of the fineness of a powder, comparison of the result for M-10 and M-20 in Table 10 shows that the Turbidimeter yielded analyses which were consistent with the burning time data, that is, M-10 is a finer powder than M-20. The Micromerograph showed a smaller difference between these two lots. The Coulter Counter gave results which were inconsistent with the burning times. It showed both powders to be quite coarse, as indicated by the small surface area, and that of the two, M-20 is finer. The B.E.T. nitrogen adsorption method also indicated coarse powders and failed to show any difference between the two lots.

Since the burning times for compns burning in the 40 sec/inch range may vary by as much as 3–5 seconds from batch to batch, the difference in burning times for tungsten samples ND3499 and ND3657 cannot be significantly related to the difference in particle size. However, the differences in burning time between these coarse powders and the finer M-10 and M-20 is readily apparent.

A comparison of the distribution curves given by the Turbidimeter, Micromerograph and Coulter Counter for identical samples of tungsten is shown in Figure 20.

![Graph](image)

Fig 20 Size Distribution Curves for Three Methods of Particle Size Analysis — Tungsten M-10
Table 11
Precision of Eagle-Picher Turbidimeter Experimental Work

<table>
<thead>
<tr>
<th>Tungsten Lot</th>
<th>Sample No.</th>
<th>Specific Surface cm²/gm</th>
<th>Standard Deviation cm²/gm</th>
<th>Percent of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-10*</td>
<td>2</td>
<td>1802</td>
<td>13.6</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1789</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-20*</td>
<td>4</td>
<td>1056</td>
<td>58.7</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1171</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1093</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ND 3499**</td>
<td>13</td>
<td>694</td>
<td>9.2</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>681</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ND 3657***</td>
<td>14</td>
<td>558</td>
<td>7.1</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>548</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Samples obtained from Sylvania Products, Inc.
** Samples obtained from Fansteel Corp

The lack of fines shown by the Micromerograph was probably due to the excessive “hang-up” which has been reported. The extreme coarseness of the results given by the Coulter Counter is unexplainable, however, inadequate deagglomeration could produce this effect.

The time required to determine a complete size distribution curve on the Turbidimeter and the Micromerograph varies with the fineness of the particulate material. The longest time involved in obtaining a size distribution curve for the finest sample of tungsten was 2½ hours. The time for analyzing a comparable powder on the Micromerograph was 5 hours; however, 4 hours of this was necessary to allow the sample to settle. Since the Micromerograph recorder is automatic, the operator time is reduced accordingly. It is also possible to adapt a recorder to the Turbidimeter, and thus further reduce the operator time for this technique.

Table 11 shows the precision obtained with the Eagle-Picher Turbidimeter. Column 4 is the standard deviation of the specific surface values, and column 5 gives these as percentage of the mean specific surface values.

An indication of the reproducibility of the Turbidimeter is shown in Fig 21.

The results of the microscopic particle size determination are shown in Fig 22.

The number-size distribution of the microscopic determination was converted to a weight-size distribution for comparison with the weight-size distributions given by the Turbidimeter and the Micromerograph for the same material. As shown in Fig 22, which is a log-probability plot, there seems to be no correlation; this is probably due to the effect of the extremely small samples which are used in the microscopic method. This presents problems of obtaining a representative sample and complete deagglomeration.

The turbidimetric method as exemplified by the Eagle-Picher Turbidimeter seems to offer a convenient and fairly rapid method for control or laboratory use, and the precision and reliability seem adequate. A small concn of sample is sufficient so that particle interference and reagglomeration tendencies are negligible, in contrast to other sedimentation methods which require larger samples.
Fig 21  Reproducibility of Turbidimeter – Tungsten ND 3657
Fig 22  Comparison of Microscopic Method of Particle Size Analysis — Tungsten M-10

**Sedimentation Balances**

These instruments, sometimes referred to also as sediment accumulation devices, weight the sediment as it accumulates on a weigh-pan at the base of the sedimentation column. The methods are cumulative ones. With the development of sensitive electro balances, the cumulative sedimentation technique is generally easier to perform and more accurate than is the incremental technique. The powder may be dispersed initially in the bulk of the fluid or added instantaneously at the top. An advantage of this type of equipment is the absence of the conical base, needed in sediment extraction devices, upon the walls of which some sediment may adhere. The danger of particles sticking to the vertical walls is however still present.

**CAHN RG ELECTROBALANCE/SEDIMENTATION ACCESSORY.** This app produces a continuous, visible chart record of the sediment weight collected on the balance pan. It has been evaluated for measuring particle size distributions of the primary expls Lead Styphnate, Lead Azide, & Tetracene by Hutchinson (Ref 41). It is difficult to obtain accurate particle size analyses of primary expls because (1) consideration and acceptance of necessary safety precautions make the usually tedious job of particle size analysis even more tedious, and (2) many primary expls used in production contain particles which are non-spherical in shape and are in the subsieve size range. Dry screening Lead Azide, for instance, is hazardous and must be done remotely. Furthermore, static charges...
tend to cause the formation of agglomerates, and erroneous results are obtained. Wet screening is tedious, and it is very difficult to remove all the very fine particles from the coarser particles when fine, non-spherically shaped particles are encountered. The apparatus is shown schematically in Fig 23.

Four samples of Lead Stypnate were analyzed by dispersing in acet and were found to have average diameters of 15.9 μ with a standard deviation of ± 0.4 μ. The reproducibility for Tetracene, with average diameter of 35 μ, was ± 2 μ. Methanol was found to be a satisfactory dispersant for Lead Azide with average particle diameter of 12 μ.

PERMEABILITY TO FLUID FLOW

The relevance of methods in this section to the measurement of specific surface depends on certain relationships that are assumed to hold between the rate of fluid flow, the pressure head, viscosity of the fluid, density and specific surface of the powder, and porosity of the powder bed. Generally the relationship assumed is the Kozeny equation or some modification of it:

\[ u = \frac{Q}{A} = K_1 \cdot \frac{\Delta P}{nL} \]  

(17)

where:
- \( u \) = apparent linear rate of flow in cm/sec
- \( Q \) = rate of flow in ml/sec
- \( A \) = cross-sectional area in cm²
- \( K_1 \) = proportionality constant representing the permeability of the porous medium
- \( \Delta P \) = pressure difference driving the fluid thru the medium, in g/cm²
- \( n \) = viscosity of the fluid in poises
- \( L \) = thickness of the porous medium, cm

Since the permeability of the bed is the property that is measured, the validity of the estimates of specific surface derived therefrom de-
pends on the validity of the relationships assumed. The methods give useful comparisons between different samples of materials of the same type, and hence are frequently used in control of raw materials. Anomalous results may be obtained if materials with widely divergent size or shape distributions are compared; the results of permeability measurements should therefore be interpreted with due caution.

**Gas Flow**

**FISHER SUB-SIEVE SIZER.** The app consists of a cell, a manometer and a flowmeter. The powder to be measured is compacted into a bed in the cell and dry air is allowed to flow thru it under a constant pressure differential, the rate of flow being measured. A diagram of the mechanics of the system is given in Fig 24.

Air flows thru a calcium drying tube and then downward thru the sample tube, in which the powder is supported by a porous plug. The air then passes thru a column of compacted fine sand situated between the upper ends of the two arms of a water-filled manometer. The manometer and the resistance formed by the sand column together constitute a flowmeter, while the manometer, in showing the pressure drop across the sand column, gives by difference, the pressure drop across the other resistance, the powder sample.

Since the air passes thru a resistance flowmeter, the pressure on the downstream side of the bed varies with the rate of flow. When the manometer across the flowmeter becomes steady, the reading is taken, and the surface area and “average particle size” (APD) are obtained from a family of curves on a chart incorporated in the instrument. Despite its limitations, the Fisher Sub-Sieve Sizer has been the instrument of choice for measurement of energetic materials in the sub-sieve range (2 to 50 microns) (Refs 13, 21 & 24). It is fast, but provides only a single measurement, the APD. The use of the APD tends to obscure the fact that in practically every case the sample is not a uniform material, but is instead, a mix of particles whose diameters cover a range of sizes. Because of the principle on which the Subsieve Sizer is based, the APD is a “surface average” and should be distinguished from “number averages” and “weight averages”.

The detn of APD’s between 100 and 500 microns can be made using a permeability app larger than the Fisher Sub-Sieve Sizer. This app, which was developed at PicArsn, uses a sample size of approx 10 times the sample density (Ref 7a).

![Diagram of Air Permeability Apparatus](image)

Fig 24 Air Permeability Apparatus
ADSORPTION METHODS

There are various methods for the determination of the surface area of solids based on the adsorption of a mono-, or polymolecular layer on the surface of the solid. These methods do not measure the particle diameter or projected area as such, but measure the available surface per gram or milliliter of powder. The surface measured is usually greater than that determined by permeability methods as the latter are effectively concerned with the fluid taking the path of least resistance thru the bed, whereas the adsorbate will penetrate thru the whole of the bed as well as pores in the powder particles. These methods appear to be more accurate than surface areas calculated from “weight averages” or “number averages” of particle size because cracks, pores, and capillaries of the particles are included and are independent of particle shape and size.

Static: Involving Use of Adsorption Isotherms

BRUNAUER, EMMETT, AND TELLER (B.E.T.). In this method the surface area is not measured directly, but the number of molecules of the adsorbed substance required to give a monolayer (N) is determined. If the mean area per molecule (σ) of the adsorbed substance is known by other means, the area of the solid may be calculated as:

\[ e = N \sigma \]

The method uses the adsorption isotherm and the expt details of determining this may be summarized as follows: (1) the powder under investigation is thoroughly degassed in a vacuum; (2) a small amount of gas or vapor is added at constant temp; (3) the resultant pressure is noted; with no solid present, the pressure would follow the gas laws; with powder present, the pressure is lower; (4) a curve of volume of gas admitted vs pressure is prepared; and (5) from this isotherm, the surface area may be determined.

Harkins and Jura (Ref 5) have described an improved modification of the basic B.E.T. method for the calculation of surface area. Eigsti & Dwiggs (Ref 16) evaluated this method for the determination of the particle size of chemical delay comps vs other methods, as described earlier in this article (see Table 9).

Dynamic

SORPTOMETER (PERKIN-ELMER). This method is essentially a gas-chromatographic technique with the sample powder in place of the normal chromatographic column. A mixt of He and N₂ is passed thru the sample and the concn of N₂ in the exit gas is measured by thermal conductivity or gas-density methods.

### Table 12

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Surface Area Measurements (M²/gm)</th>
<th>Graphical Surface Area (M²/gm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microscope</td>
<td>Micromerograph</td>
</tr>
<tr>
<td>0-10µ Al</td>
<td>S_cal (1)</td>
<td>S_vs (2)</td>
</tr>
<tr>
<td>0.444</td>
<td>0.208</td>
<td>0.379</td>
</tr>
<tr>
<td>10-20µ Al</td>
<td>0.161</td>
<td>0.131</td>
</tr>
<tr>
<td>20-30µ Al</td>
<td>0.105</td>
<td>0.097</td>
</tr>
<tr>
<td>30-40µ Al</td>
<td>0.094</td>
<td>0.093</td>
</tr>
<tr>
<td>40-50µ Al</td>
<td>0.077</td>
<td>0.077</td>
</tr>
<tr>
<td>Alco-123 Al</td>
<td>0.299</td>
<td>0.102</td>
</tr>
</tbody>
</table>

(1) S_cal = Surface area calculated from microscopic data
(2) S_vs = Surface area per unit volume
(3) S_s = Specific surface area
(4) S_w = Specific surface area by the parameters of the weight distribution

* From Log-Probability Plots
and plotted on a recording potentiometer. The change in N₂ content of the exit gas when the sample is cooled in \textit{liq} N₂ gives a measure of the quantity of N₂ adsorbed on the sample surface. The adsorption measurement is repeated, with three or four different concns of N₂ in the He, and the surface area of the sample is calculated from the B.E.T. equation \( e = N_0 \).

Johnson, Christian, and Tiedemann (Ref 27) evaluated the Sorptometer vs the Micromerograph and the microscope for particle size and surface area determinations to characterize powdered materials used in solid propilts. Table 12 compares the surface area of Al powder samples calculated from Micromerograph and microscopic data with that measured using a Sorptometer.

Sorptometer measurements ran higher in 8 of the 12 lots of Al tested, apparently reflecting the area measurements of the pores, cracks and capillaries of the material and irregular shapes. Similar comparisons obtained with samples of Ammonium Perchlorate are summarized in Table 13.

Both the Al and AP samples appeared to follow very closely the log normal law of particle distribution as evidenced by the straight line plots of the size distribution data obtained microscopically and Micromerographically. This appears to be typical of dispersions obtained by milling, crushing, or grinding.

Sulcer and Denson (Ref 19) used the gas chromatographic-B.E.T. procedure for the analysis of Class I Al powder (45\( \mu \), max dia) which cannot be tested satisfactorily by sedimentation methods because of the presence of aggregates. A rough statistical evaluation of this procedure was made by running twelve determinations and calculating the standard deviation as shown in Table 14:

### Table 14

**Specific Surface of Class I Aluminum Powder**  
**Lot Number 1457**

<table>
<thead>
<tr>
<th>Specific Surface, cm²/g (Nitrogen Adsorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6401</td>
</tr>
<tr>
<td>6245</td>
</tr>
<tr>
<td>5220</td>
</tr>
<tr>
<td>5518</td>
</tr>
<tr>
<td>5855</td>
</tr>
<tr>
<td>5842</td>
</tr>
<tr>
<td>6049</td>
</tr>
<tr>
<td>5922</td>
</tr>
<tr>
<td>5744</td>
</tr>
<tr>
<td>6054</td>
</tr>
<tr>
<td>6041</td>
</tr>
<tr>
<td>5421</td>
</tr>
<tr>
<td>5859 Average</td>
</tr>
<tr>
<td>670 Standard Deviation</td>
</tr>
<tr>
<td>3759 Specific Surface by Micromerograph</td>
</tr>
</tbody>
</table>

### Table 13

**Ammonium Perchlorate Surface Area**

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Surface Area Measurements (M²/gm)</th>
<th>Graphical Surface Area (M²/gm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microscope ( s_{cal} )</td>
<td>Micromerograph ( s_{vs} )</td>
</tr>
<tr>
<td>P-Lot No 13 AP</td>
<td>0.226</td>
<td>0.250</td>
</tr>
<tr>
<td>A-28 AP</td>
<td>0.394</td>
<td>0.179</td>
</tr>
<tr>
<td>5 AP</td>
<td>0.530</td>
<td>0.404</td>
</tr>
</tbody>
</table>

(1) \( s_{cal} \) = Surface area calculated from microscopic data  
(2) \( s_{vs} \) = Surface area per unit volume  
(3) \( s_{s} \) = Specific surface area  
(4) \( s_{w} \) = Specific surface area by the parameters of the weight distribution

* From Log-Probability Plots
The Sopptometer appears to offer several advantages for use in determining the surface area of fine powdered proplnt ingredients. By comparing the specific surface determined by N₂ adsorption with the specific surface determined by other methods, an estimate of the deviation of the particles from a sphere can be made. For many very fine powders, N₂ adsorption is one of the few methods available for describing the size of the particles.

**IMAGE FORMATION**

In methods involving image formation there is a common factor. Radiation normally propagated in rectilinear fashion, such as light or an electron beam, is interrupted by the particles under examination, and the pattern of the interruption can be observed in different ways, e.g., optically or photo-electrically.

**Light Beam: Optical Microscope**

The image produced may be viewed either directly by the eye or projected on to a screen. The latter method is usually the more convenient and involves less eyestrain; it is less satisfactory than direct observation for fine sizes near the limit of optical resolution. Sizing is commonly achieved by comparison of the particle images with a scale or graticule. Since the process is tedious, sizing is sometimes performed automatically. The smallest resolvable particle size is a function of the wavelength of the light used and varies between 0.5 and 1μ.

The optical microscope has the advantage that it is direct and the analyst examines his material himself, so that he can appreciate changes in shape and size and especially the state of aggregation of his sample, factors not always appreciated in an indirect method of analysis. Nevertheless, judgments are involved and the method is undoubtedly tedious, so that results may vary even in the hands of experienced operators. The method is also very time consuming in the requirements for counting a sufficient number of each sized particle for statistical accuracy. One of the biggest problems is that of obtaining a truly representative sample due to the comparatively small amount of sample capable of being dispersed in the microscopic field of view.

**Light Beam: Flying-spot Principle**

The difference between this principle and that of the optical microscope methods is that the whole field is not illuminated simultaneously, but is scanned by a fine light spot. Interruption of the illumination is measured electronically.

**RANK CINTEL INSTRUMENT.** A moving spot of light, produced on the face of a cathode-ray tube, is focused on the sample by means of a suitable lens system. The amount of light passing through or reflected from the sample varies according to the optical density and configuration of the individual particles of the sample. These changes in light intensity are detected by a photomultiplier, the signal from which is fed into counting and sizing circuits. A memory device prevents each particle of the sample from being counted more than once, and sizing is accomplished by pulse subtraction.

The instrument has been evaluated by Luster, Whitman, and Fauth (Ref 20). They selected atomized Al, AP and NGu as materials for study that would be representative of proplnt ingredients. They found that only 2000 particles could be counted in 2 hours, a time arbitrarily chosen as feasible for control work. This number is not considered sufficient, as 18,000 particles are required for a 95% confidence level. Statistical analysis of results obtained for AP was impossible because of discrepancies in the data resulting from crystal growth and particle agglomeration. The sample of NGu could not be handled by the instrument because it consisted of a mix of needles and chunky particles. They concluded that for dimensionally stable materials such as Al or carborundum, excellent agreement was found with other methods such as the Micrometerograph or visual microscopic count. But because of the properties peculiar to AP and NGu, the Flying Spot Particle Resolver was not believed suitable for process control of these materials.

**ELECTRON MICROSCOPE.** The use of an electron beam in place of light gives the electron microscope a much greater magnifying and resolving power than the optical microscope so that particle diameters of 0.001 to 20μ may be measured when special precautions necessary for preparing the sample and for calibrating the magnification are observed.

Suspensions of particles may be examined
after either depositing them on a very thin membrane, or incorporating them into it. For most purposes, the deposition method is preferable, but when it is necessary to draw particle size distribution curves, the incorporation method is more convenient. Membranes are usually made from plastics (collodion, Formvar, polystyrene, etc) or from extremely thin films of light metals (Be or Al) or oxides (SiO₂) formed by deposition. A photomicrograph is produced of the incorporated or deposited particles which can then be treated in just the same way as a photograph produced by the optical instrument. A recent development is Scanning Electron Microscopy (SEM) which is similar in effect to the flying-spot microscope.

Kuentzmann (Ref 43) has applied the SEM to the study of the condensed phase of the combustion products of metallized solid propellants. The aluminum oxide particles in the rocket exhaust were collected on glass plates, metallized under vacuum (the thickness of the metal depositions being negligible when compared to the particle diameter) before being placed on the plates of the SEM. Manual counting using a sliding caliper was found more satisfactory than automatic data reduction.

**ELECTRICAL PROPERTIES**

**COULTER COUNTER.** This commercially available equipment utilizes the change in resistance of the system caused by the presence of a particle suspended in an electrolyte. The susp-

---

**Table 15**

Comparison of the precision of the Sharples Micromerograph with that of the Coulter Counter using standard glass bead sample, type XC-3

<table>
<thead>
<tr>
<th>Geometric Means</th>
<th>Standard Deviations of Distributions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Micromerograph, microns</td>
</tr>
<tr>
<td></td>
<td>By Weight</td>
</tr>
<tr>
<td>13.8</td>
<td>8.9</td>
</tr>
<tr>
<td>14.3</td>
<td>8.9</td>
</tr>
<tr>
<td>13.8</td>
<td>9.0</td>
</tr>
<tr>
<td>14.2</td>
<td>7.6</td>
</tr>
<tr>
<td>14.2</td>
<td>9.4</td>
</tr>
<tr>
<td>15.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Averages</td>
<td>14.2</td>
</tr>
<tr>
<td>Standard Deviations</td>
<td>±0.4</td>
</tr>
</tbody>
</table>

Coulter Counter operational conditions:
- Gain index: 4
- Aperture: 100 microns
- Electrolyte: 1% aqueous NaCl solution
- Sample weight: 25 mgs

Micromerograph operational conditions:
- Deagglomerator: 250 microns
- Pressure: 100 psi
- Sensitivity: 1
- Sample weight: 40 mg

* By Count — Micron sizes by weight were converted to micron sizes by count using the following equation:

\[ \ln D_n = \ln D_w - 3 \left( \ln \frac{D_w}{D_w^{50\%}} \right)^2 \]

where:
- \( D_w \) = particle diameter by weight at percentages shown above
- \( D_n \) = particle diameter by count at percentages shown above
- \( D_w^{50\%} \) and \( D_w^{16\%} \) = particle diameters by weight at 50% and 16% points respectively
pension of particles flows thru a small aperture having an immersed electrode on either side, with particle concn such that the particles traverse the aperture substantially one at a time. Each particle passage displaces electrolyte within the aperture, momentarily changing the resistance between the electrodes and producing a voltage pulse of magnitude proportional to the particle volume. The resulting series of pulses is electronically amplified, scaled and counted.

Elgisi and Dwiggs (Ref 16), as reported earlier in this article, compared the Coulter Counter with other methods for the particle size analysis of powdered W (Table 10). Subsequently, Middlebrooks, Kaye, Edelman, and Wein- garten (Ref 30) evaluated the instrument with spherical glass beads. They found that in the range of 0-30\(\mu\), the Coulter Counter can evaluate spherical glass bead distributions with greater precision than can the Sharples Micromerograph. Geometric means and standard deviations for the Counter were found to be 0.4\(\mu\) and 0.03\(\mu\), respectively, while the geometric means and standard deviations for the Micromerograph were found to be 0.4\(\mu\) and 0.04\(\mu\), respectively, as shown in Table 15.

The accuracy of the Coulter Counter over the range 0-30\(\mu\) is poor when compared with microscopic data. The instrument yields geometric mean values which are far coarser than those obtained microscopically. Proportionately smaller size differences are indicated as the distribution curve extends from the geometric mean toward the coarse tail, and proportionately larger particle size differences are apparent as the curve proceeds from the geometric mean toward the fine tail. This effect is shown in the plot comparing Coulter Counter data with microscopic data, Fig 25.

H.L. Stalcup (Ref 28) evaluated the instrument for the particle size determination of HMX used in rocket formulations. He found that Coulter Counter distribution was similar to that obtained with the Micromerograph except at the large particle end, where the Micromerograph indicated particles over 100\(\mu\) compared to 32\(\mu\) for the Coulter Counter. Median values were 13.5\(\mu\) by Micromerograph and 16\(\mu\) for the Coulter Counter. The samples for the Coulter Counter were run on an "as received" basis, ie, while still water-isopropanol wet; whereas, it was necessary to completely dry the samples prior to analysis by Micromerograph.

In the latter case the possibility for particle size changes exists due to agglomeration or crystal growth. They found that the instrument is capable of measuring particles from 250 microns down to 0.2 microns by using the proper sized aperture. To prevent plugging, the largest particle diameters in a sample should be no greater than 45% of the diameter of the aperture. It is necessary to find a suitable liq electrolyte for dispersing the sample that is non-dissolving, non-agglomerating, and non-settling. Murphey, Day, and Dillehay (Ref 29) evaluated the instrument for particle size analysis of AP used in solid propmts. The biggest problem in this case was finding a suitable electrolyte. A 2:3 mix of benz and n-butanol satd with lithium chloride was found to best satisfy the electrolyte requirements for this material. It was then found that the Coulter Counter was more precise than the Micromerograph in providing data from which to calculate average diameter and specific surface values. Five different samples of AP were chosen to cover a wide range of particle size distributions. Each sample was analyzed five times on both the Micromerograph and the Coulter Counter. The standard deviations found were:

<table>
<thead>
<tr>
<th>Specific Surface cm(^2)/g</th>
<th>Diameter (\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulter Counter</td>
<td>48.9</td>
</tr>
<tr>
<td>Micromerograph</td>
<td>129.0</td>
</tr>
</tbody>
</table>

These data reflect the relative precision of the systems and not the accuracy of either system. It was found essential to maintain cleanliness around the Coulter Counter at all times. Dust and moisture must be avoided or high background counts and instability will result. The Coulter Counter analysis was found to be more rapid than the Micromerograph, requiring approximately 15 minutes per analysis as compared to 90 minutes for high surface material on the Micromerograph. The use of a multichannel Coulter Counter would reduce the time per analysis to less than five minutes.

**QUADRUPOLE RESONANCE.** This concept is based on the theory that the quadrupole resonance frequency of the chlorine nucleus in AP will vary with the particle size. This is because...
Fig 25 Comparison of microscopic particle size distribution with the average distribution of four tenets.

- 2.6 microns
- 11.2 microns
- 32.2 x 5 x 5 % weight loss from diameter

Particle size, microns

- Geometric mean
- Standard deviation of
- Distribution of
- Microscopic mean
- Geometric mean
- 0.71 distribution

(32.2 x 5 x 5) excluded particles
The microscopic modification

% weight loss from diameter
the internal electric field of a crystal will vary with its particle size, when very small crystal sizes are involved. This variation of internal electric field will cause a shift in the quadrupole resonance frequency. Since extremely small changes in frequency measurements can be made, it is believed that extremely small changes in frequency due to particle size variation can be detected. By determining the amplitude of the quadrupole resonance signal at a range of frequencies, and calibration against known standards, the particle size and distribution could be measured.

Wachtell (Ref 23) worked on the application of this principle. However, early in his work a major problem was encountered in finding the quadrupole resonance of the chlorine nucleus which did not exist in the frequency range in which it had been expected (20–40 megacycles). Nuclear Magnetic Resonance studies finally have shown that this quadrupole resonance should exist around 150 kilocycles. Future studies of single crystals of AP should reveal the presence and the exact location of this resonance. If this can be done, then the analysis of particle size, based on the shift of the quadrupole resonance frequency, may be possible.

**Written by D. J. VEAL**

41) R.W. Hutchinson, "Use of Liquid Sedimentation Techniques for Measuring the Particle-Size Distribution of Primary Explosives", PATR 4387 (1972)
42) Anon, "Standard Method for Subsize Analysis of Granular Metal Powders by Air Classification", ASTM B 293-60 (1973)
43) P. Kuentzmann, Recherche Aerospatiale, 71 (1973)
44) G.M. Shiflett, "Particle Size Investigation of Polyox WSR 301 Polymer Powders Using a Turbidity Technique", NSRDC 28-621 (1973)
46) D.J. Freeman, "Particle Size Measurement of Components of Pyrotechnic Delay Compositions", PATR 4693 (1975)

Partridges (Partridge Mortars). Large artillery mortars once used in sieges and in defensive fortifications. They had a central bore for a normal shell, which was ringed by 13 smaller bores for firing grenades

155mm gun weighed 1g each, and were about 2mm thick and 15mm in diameter. Two or three hundred of these were sewn up in a silk bag, which was loaded into the gun along with the bag containing the propellant, such as Poudre B. The pellets burned with nearly the same velocity as the propellant, and had practically no effect on the ballistics. They produced a certain amount of smoke, and the discharge gave a red glow from the muzzle of the gun
Ref: Davis (1943), 326

Patch. A piece of greased cloth or leather which was wrapped around the ball to make it fit the bore more tightly. It was commonly used with muzzle-loading rifles that fired spherical balls, and in some dueling pistols.
A second meaning is that of a small piece of cotton cloth used to clean the bore of small arms

Pâte Explosible. Early Fr Dynamite contg NG 72, Mg carbonate 20, chalk 6 & sawdust 2%
Ref: Daniel (1902), 601

Patent Blasting Powder. Early safety mining expl, consisting of BlkPdr to which ordinary salt was added to lower the deflagration temp
Ref: Daniel (1902), 601

Patent Gunpowder. Smokeless powder based on Nitroglycin, manufd in the 1870's at Clyne-Ceirorg, Wales. The expln of the ship Great Queensland in 1876 was attributed to impurities in this propellant which caused spontaneous combustion
Ref: Daniel (1902), 601

Pastilles Antilucreurs (Fr for Antiflash Pellets). Pellets of a compressed intimate mixt of 4p of K nitrate and 1p of DNT, used during WW1 in lieu of Sachets Antilucreurs (qv) or other flash reducers. For example, pellets used in the

Patton Explosives. Chlorate expls to which flour or bran was added to diminish the sensitivity. They were patented in Eng in 1880
( BritP 810)
Refs: 1) Daniel (1902), 601 2) Guina, Trattato 6 (1959), 393
Paul Cartridge. This cartridge was invented by a Swiss gunsmith, Pauli, residing in Paris, and submitted to Napoleon I in 1812. It was the first cartridge in which metal was used; and resembled the present "shotgun" cartridge. It consisted of a brass base in the form of a rosette, to which was attached an envelope of combustible paper containing a charge of BlkPdr. A pellet of primer compn was placed between the base (rosette) and the proplnt charge. The design of the cartridge, very different from anything existing at the time, was not understood by Napoleon and his advisors, and no use was made of it until it was reinvented about 40 years later by other gunsmiths.


Paulilite’s Gray Dynamite. Consisted of 20–25% NG mixed with Na nitrate, resin and charcoal
Ref: Daniel (1902), 362

Paulilite’s White Dynamite. Consisted of 70–75% NG absorbed on 30–25% natural siliceous earth
Ref: Daniel (1902), 73

Paul’s Chronograph. A modification of Duda’s Ballistograph for detg the velocity of projectiles in flight. See under Ballistograph in Vol 2, B10-L

Payload. Generally, that part of a load that is expendable, deliverable, or ready for use in direct accomplishment of the mission. The warhead, its container, and activating devices in a military missile. The satellite or research vehicle of a space probe or research missile

PBX. An acronym for Plastic Bonded Explosive. A term applied to a variety of expl mixts which are characterized by high mechanical strength (above 10,000psi compressive strength), good expl properties (usually > 7800m/sec deton vel), excellent chemical stability, relative insensitivity to handling and shock (to extremes of from 10 to 40% above that detg the basic expl), and high thermal input insensitivity (average autoignition temp > 250°). These expl mixts contain a large percentage of basic expls such as RDX, HMX, HNS or PETN in intimate mixt with a polymeric binder such as polyester, polyurethane, nylon, polystyrene, various types of rubbers, NC, or Teflon. In some instances a plasticizer such as dioctylphthalate (DOP), DPA or butyldinitrophenylamine (BDNPA) is included in the ingredients as well as a fuel such as Al or Fe powd. Available PBX compns and parameter information are shown in Tables 3, 4 and 5

Much of the advantage stemming from the use of PBX compns lies in the simplicity of the technique of end item manuf. About half of the developed PBX compns are used to directly cast end items (see Table 1 for examples). For this proc no elaborate melting equpt or controlled cooling cycles are reqd. All operations may be conducted at ambient temps and, in some instances, can even be carried out in the field (Ref 38). However, where extraordinary mechanical strength is required or where complicated shapes are desired, a pressng or injection technique is applied using a molding powd or slurry of the PBX (see under Mfg of PBX Type Expls) (Refs 10, 15, 64 and 73). The final PBX product not only exhibits excellent technical props but also has the economical advantages of low processing costs, the ready availability of all constituents from commercial sources and, (in currently evolved compns) an ease of recycling or disposal because of the use of thermally degradable binders (see under History)

History. The first attempts to desensitize RDX were reported by Frankel and Carleton (Refs 1 thru 5) who made use of polymeric materials such as polyurethanes to coat expl cryts by means of emulsion or soln techniques. The first true PB-RDX was developed in 1952 at the Univ of Calif’s Los Alamos Lab and consisted of RDX coated with polystyrene plasticized with DOP (Refs 6 & 21). Since then the Lawrence Livermore Lab has evolved a series of PBX formulations, many of which are listed in Tables 3, 4 & 5. These compns are described in Ref 77
(and are so referenced in the Tables) and are identified by their nomenclature code prefixes as to their state of development; viz. "PBX-..." indicates a prodn expl compn; expls which have reached the stage of being ready for routine mfg are designated "LX-..."; while research compns are called "X-...", as "XTX-8003". However, much of the work on mil PBX compns has been under the aegis of the US Navy (Refs 10-14, 16, 20-33, 35-38, 40, 43, 44, 50, 53b, 55, 60, 64, 66 & 72). The first formal ordn development program was initiated in Aug of 1954 by the BuOrdn for airt-o-air rocket missile (Gimlet) warhead to be developed by the Navy. This program resulted in the development of the PBXN series, also tabulated in Tables 3, 4 & 5. HMX based expls for projects such as the 8" arty fired atomic proj and the Lunar seismic expls were evolved during the 1960's and early 1970's using Teflon as the binder (Refs 51, 55, 60, 67 & 69).

Development work by the US Navy has included attempts to use expls other than RDX and HMX; viz., HNS and TACOT (Tetranitrotoluene, 2,5,6-triazido-1,2,5,6-tetrazadibenzo-cyclooctatetrene) together with binders such as RTV silicon rubbers. As reported by Stott (Ref 43) such work was not fruitful because of the low detovel and d of the developed compns.

One of the problems arising from the use of PBXs is their disposal or recycling. This problem is, of course, a common one with all munitions. The work of Sitzman et al (Ref 66) provides a technique to recycle or dispose of munitions safely by means of an expl solvent-pump-expl recovery system. A butylroactone-dimethyl sulfoxide mixt (73/27%) is recommended for PBXs containing a large amt of HMX. However, no solvent was found that disintegrated PBXs (such as PBXN-101 and PBXW-106) containing cast-cured cross-linked polymers. The solution to this problem, as decided upon by the US Navy, was to develop a thermally degradable PBX series. This solution at first glance appears to be almost a complete turn-about in the philosophy of the ultimate PBX being completely heat insensitive. However, this requirement, as expressed in a NavSeaSystCommand Contract to Stanford Research Inst of Calif (Ref 71), was to evolve PBXs (and other expl ordn items) that would undergo controlled thermal degradation so as to yield material that could be easily removed from expl casings for the purpose of efficient recycling of the base expl, or for low pollution disposal of the entire item. SRI's Ross et al accomplished a portion of this goal by using a polypropylene-glycol-urethane polymer to prepare an HMX-based PBX. Upon heating the developed PBX at 160° for 10 hrs, the binder decomps to a readily sol material, and the HMX was quantly recovered. It is predicted that by 1979 this nonpolluting recycling technique will not only supplement expl solvation procedures, but will also displace both burning and sea disposal of ordnance to a great degree.

Available data on mil in-house or contractor developed compns are presented below using USA mil specs as well as tabular format (Tables 3, 4 & 5).

There are more than several PBX compns developed outside of the USA or by USA non-military organizations which are of interest and are presented here. The PBX developed by Wright (Ref 41) is a molding powd prepd by mixing a w dispersion of a binder such as a polyacrylate, a plasticizer such as paraffin oil, with w slurry of an expl such as RDX and a coagulant such as ethanol. Hard, well-formed granules are produced which contain 90-98% expl. Subsequent pressing at 25000psi and 120° yields pellets with a compressive strength of 10000psi. In an expl patented by Wright (Ref 44a) much the same procedure is followed using, in this instance, poly (hexamethyleneadipamide) as the binder and Diphenylaminonitrobenzene as the expl. The prod contains 90-98% expl with a bulk d of 0.6-0.7g/cc.

Sato (Ref 44b) reported the development of a PBX series using PETN and a combination of Epikote 871 (an epoxy resin) copolymerized with diethylenetriamine in percent ratios of 70/30, 65/35 and 60/40 (expl/binder). The compresion strength of this expl series avg 60kg/sq cm. Vacek and Skrivanek (Ref 52) invented a series of PBXs using an aq dispersion of poly- (vinyl acetate) binder, PETN as the expl, with dibutylphthalate as the plasticizer in a typical wt% ratio of 36/60/4. A typical deton rate is 5200m/sec using a 28mm charge diam with a d of 0.92g/cc. A self-supporting PBX
series has been developed by Minekura et al (Ref 58) which can be fabricated in plate, strand or tape form for use in metal forming by impulsive loading. The compn can include polyethylene as binder, a paraffinic hydrocarbon as plasticizer, and an expl-oxidizer combination. The development of PBX comps using a polyester as the binder and RDX as the expl has been reported by Reichel in Ref 76. Evans (Ref 70) invented a PBX series with comps using, for example, PETN as the expl, a polyethacrylate rubber as the binder, and dibutylphthalate as the plasticizer in wt% ratios of 60-85/10-40/0-10. A typical product detond with a No 6 elec blasting cap at a rate of 8180m/sec. In another PBX series, that of Butler et al (Ref 68), β-hydroxyethyl acrylate is the binder, ethylene glycol is a copolymer, benzoyl peroxide is the catalyst, while LiClO₄ is the oxidant, and RDX or HMX is the base expl. A typical wt% ratio is 20/13/1/9/57. An invention of Kegler et al (Ref 84) has increased the pot life (before molding) of PBX comps contg 5-15% polyester binder by several days thru use of gelatin microcapsules to inclose the benzoyl peroxide. The catalyst is released during the pressure-molding operation. Frankel et al of Rockwell Intl Corp (Refs 80 & 81) developed a series of nitrofluoroalkyl epoxides (epoxy ether expls) which are heat and impact stable and are used as binders with RDX (80%) as the expl. For available parameter data see Tables 3 & 4. A flexible, self-supporting PBX was patented by Rothenstein (Ref 83) which uses fine-particle expl in admixt with low d prepolymer.

For example, using hydroxy-terminated polybutadiene as the binder, RDX as the expl, toluenediisocyanate as a co-polymer, sym-di(2-naphthyl)-p-phenylenediamine as an antioxidant, and polybutene as the plasticizer in a wt% ratio of 12.1/42.7/5/0.2/40, a castable expl is produced.

Manufacture of PBX Type Explosives. Several mfg procedures are currently used to produce PBXs. One of these techniques is that of casting. (Fig 1 illustrates a process for PBXN-101). This procedure, at first glance, merely involves combining a dried expl, such as HMX, with binder constituents and curing initiators in a mixing vessel, blending to desired homogeneity, then casting into a given warhead or other ordnance item. Unfortunately, there are hazards associated with the drying of large quantities of expls such as HMX or RDX. Hence, a desensitizing procedure must be added for production-scale operations. This procedure involves coating the HMX (or RDX), w-wet as normally stored and shipped, with the alkyd or polyester portion of the binder. The resulting lacquer is added slowly to an aq slurry of the HMX (or RDX). Agitation at approx 250rpm in the presence of w causes the resin to ppt onto the surface of the HMX (or RDX), producing an insensitive powd which may be safely dried, handled, shipped, and stored until ready for use in the final PBX compn. Precoating techniques and equipment are adequately described in Refs 1 thru 7, 9, 17, 18, 22, 25, 31a, 41, 44a, 50 & 53a. The precoated expl is then mixed in a mixing kettle with sufficient copolymer to constitute the final binder compn. An accelerator (such as Co naphthenate) is added at this point. The mix is then stirred until homogeneous, at first under ambient press, and finally in a vacuum to remove entrapped air. The curing agent (such as methyl ethyl ketone peroxide) is then added. After another short mixing period (~15 min) the expl compn is poured into the desired molds. Vacuum casting has not been found necessary to obtain good density, provided that the mold design is not too intricate or the height-to-diam ratio not too great (Ref 38).
FIG 1. Flow Diagram Showing Processing Steps for PBXN - 101 Preparation
In another casting technique, that of *injection molding*, used for intricate shapes or small diam dimensions, the complete item is produced in place by relatively low press-forcing of an expl-plastic mix which is then allowed to cure (Fig 2).

![Injection Loading Operation Schematic](image)

Fig 2  Injection Loading Operation Schematic

The PBX usually employed contains a high solids content expl such as PETN (PBXC-303(1), see in Tables 3, 4 & 5) which provides for steady-state deton in small cross-sectional channel or tubes (Fig 3). Indeed, this technique was developed by the US Navy to provide expl logic links of less than 0.1" in diam. As reported by Lind et al (Ref 73) the technique of injection molding involves the movement of expl material at RT into a cavity or tubing from a reservoir. This is accomplished by applying piston press (at about 12000psi) to the expl compn in the reservoir, which forces it into a cavity or tubing. When the accepting device is full, press on the piston is relaxed and flow stops. The device is then removed and set aside to allow the expl to polymerize into an elastic rubber-like solid.

A second mfg technique produces a molding powd which is *pressed* into the desired end item shape under pressures in excess of 30000psi.

Two methods have been reported for the prepn of PB-RDX for subsequent pressing. The earlier method employed a Baker-Perkins type mixer to blend the components. This procedure gave a product with good pressing characteristics. However, the molding compn was nonuniform in granulation and tended to be dusty. The slurry method of PB-RDX prepn gave a product which was uniform, free-flowing and dustless. In addition, PB-RDX granulated by the slurry method exhibited satisfactory drying, handling and pressing characteristics. The final procedure incorporating the better features found from the study of such variables as solvents, solvent/plastic ratios, lacquer addition and temp, agitation, RDX particle size distribution, dispersants and rosin additive, was as follows (Ref 7):

![Continuous Explosive Column for use With Zuni Weapon](image)

Fig 3  Continuous Explosive Column for use With Zuni Weapon
Testing Procedures for PBX's. These are covered by either the US Mil Specs presented below or individual specs developed for such compps as the PBXN's as reported by Mason (Ref 30) and Pennington (Ref 37). Chem analysis of individual materials unique to PBX's such as the binder stabilizers hydroquinone and p-tert butylcatechol are reported by Smith in Ref 36, who used Fe-o-phenanthroline in a spectrophotometric procedure at 500 millimicrons and Stott et al in Ref 38, who also used a spectrophotometric technique employing NaOH at 460 millimicrons. More current research has led to a potentiometric titration technique for RDX or HMX (Ref 78), while Werwerka et al (Ref 79) have reported on the use of gel-permeation chromatography to detect binder degradation by ascertaining the molecular size distribution.

Mechanical properties such as viscosity, plasticity and stress under load conditions affecting various PBX's have been investigated by Armanet (Ref 15), Stott (Ref 31a), Hoge (Refs 47 & 48), Garrison (Ref 49), Springer (Ref 54) and Lindman (Ref 72).

The thermal, vacuum thermal and storage stability performance of the PBX's has been reported on by Gordon in Ref 12 and also in Refs 26, 38, 51, 56 and 77. Most of the NAVORD Refs (see under Refs) have some information on these subjects relative to the subject PBX compn of each report.

There are four PBX compns for which US Mil Specs exist, viz:

PBHM. The requirements of the USA armed forces are covered by a Mil Spec (Ref 53a) which contains the following criteria: (1) the material shall be Grade II, Class B HMX (MIL-H-45444A) coated with plastic binder by a wet slurry method; (2) plastic binder gravimetrically by wt difference after extrn with toluene sdt wth HMX, 5.0 ± 1.0%; (3) HMX, by subtraction of the percent plastic binder from 100%, 95.0 ± 1.0%; (4) bulk density, by wt and vol measurement, 0.90g/cc min; (5) moisture by the Karl Fischer method, 0.10% max; (6) granulation, gravimetrically, for information purposes only, using a mechanically shaken nest of US Standard Sieves Nos 20 (850 microns), 60 (250 microns), 80 (180 microns), and 100 (150 microns).

PBX. The requirements of the USA armed forces are covered by a Mil Spec (Ref 85) which contains the following criteria: (1) type I, the molding powder shall be a mix of RDX, coated and surrounded by a homogeneous mix of polystyrene and dioctylphthalate; (2) type II, the molding powder shall be a mix of RDX and plastic plasticizer; (3) composition, as shown below:

**PBX Composition**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Type I, %</th>
<th>Type II, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX^a</td>
<td>90.0 ± 0.5</td>
<td>90.0 ± 0.5</td>
</tr>
<tr>
<td>Polystyrene^b</td>
<td>8.5 ± 0.3</td>
<td>–</td>
</tr>
<tr>
<td>Dioctylphthalate^c</td>
<td>1.5 ± 0.3</td>
<td>–</td>
</tr>
<tr>
<td>Plastic-plasticizer^d</td>
<td>–</td>
<td>10.0 ± 0.5^e</td>
</tr>
</tbody>
</table>

^a By chromic chloride-ferric alum titration to a phenosafrin end point (green to red)
^b By calculation
^c By wt difference after extrn with isopropanol sdt wth RDX
^d By calculation
^e A mixt of 91 ± 1% polystyrene, 5.0 ± 1% dioctylphthalate and 4.0 ± 1% gum rosin

(4) foreign matter, by visual inspection of the molding powder, no inclusions or particles; (5) color, pink; (6) moisture content, by wt difference after vacuum heating, 0.3% max; (7) granulation, by use of a mechanical shaker and weighing the residue retained by each sieve as shown below:

**Granulation of PBX**

<table>
<thead>
<tr>
<th>Sieve No</th>
<th>Type I %, min</th>
<th>Type II %, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 (1000 microns)</td>
<td>thru 100</td>
<td>thru 100</td>
</tr>
<tr>
<td>30 (600 microns)</td>
<td>thru 95</td>
<td>thru 95</td>
</tr>
<tr>
<td>60 (250 microns)</td>
<td>retained 90</td>
<td>retained 90</td>
</tr>
<tr>
<td>80 (180 microns)</td>
<td>retained 98</td>
<td>retained 98</td>
</tr>
<tr>
<td>100 (150 microns)</td>
<td>retained 99.9</td>
<td>retained 99.5</td>
</tr>
</tbody>
</table>

**PBXN-1.** The requirements of the USA armed forces are covered by a NAVORD Spec (Ref 50) which contains the following criteria: (1) a preproduction sample which meets specs is required; (2) a homogeneous mixt of RDX and treated Al, each coated and surrounded by nylon; (3) RDX, acet recryst fines of 25 ± 10 microns, by wt difference following extrn with hot acet, 66.0 ± 1.5%; (4) Al, Type A, Class A (JAN-A-289), by wt difference after extrn with hot methanol, 25.0 ± 1.0%; (5) Nylon, “Zytel” 61, by subtracting the percentages of RDX plus...
Forty-two and five-tenths gms of polystyrene and 8cc dioctylphthalate were dissolved in 200cc toluene in a lacquer dissolver. Steam was introduced into the jacket until the temp reached 65°. The lacquer was agitated constantly until it was ready to be added to the granulator. This lacquer contained a 1:4 ratio of plastic-plasticizer to toluene.

Four hundred and fifty gms of RDX and 4500gms of water (ratio 1:10) were added to the granulator. The agitator was set for 400rpm and the temp was raised to 75° by introducing steam into the jacket. The temp differential between the lacquer soln and the RDX/water slurry was 5–10°.

The lacquer soln was poured thru the charging funnel into the granulator. As soon as the lacquer was added, a sln of gelatin in water was added, and the mixt was agitated until the lacquer was well dispersed in the RDX slurry (approx 5 mins). Granulation took place at this point. Steam was introduced again into the jacket to distill the solvent until the temp reached 98°. Cooling water was then run into the jacket to cool the batch to 40°. The coated material from the granulator was collected on a Buchner funnel and dried in a tray at 70° for 24 hours. Temps below 70° did not furnish enough heat, but a temp of 80° produced stickiness and caking of PB-RDX.

Another (similar) procedure for preparing up to 50 lbs of molding powd is reported in Ref 32, pp 29–31.

In a typical molding procedure the molding powd is heated in a steam oven at 112° for 2–4 hrs, then pressed to shape at 120° using 30000psi with 5mins dwell time under a vac of at least 4mm. A billet of PBX is thus produced with a compressive strength of at least 10000psi (Refs 23 & 64). Heinemann et al (Ref 34) have reported the application of expl metal forming techniques to expl pressing of PB-RDX so as to increase the d of this expl. Other advantages are economy and ease of operation. To produce an end-item the press-formed billet is usually machined using w as a coolant (Ref 61). If further assembly of the expl end-item is required the machined components are usually fastened together with a phenolic type adhesive such as Plaskon 9600 (Ref 20).

Table 1 lists examples of PBX mfg techniques and applications:

<table>
<thead>
<tr>
<th>PBX Nomenclature</th>
<th>Refs</th>
<th>Mfg Techniques</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBXN-101</td>
<td>38</td>
<td>Slurry — Casting</td>
<td>Fragmentation Type Warheads</td>
</tr>
<tr>
<td>PBXN-2</td>
<td>23, 32</td>
<td>Slurry — Molding Powd — Pressing — Machining</td>
<td>Gimlet Rocket Warhead</td>
</tr>
<tr>
<td>HNS-II/Teflon</td>
<td>55, 60, 65, 67</td>
<td>Slurry — Molding Powd — Pressing — Machining</td>
<td>Lunar Seismic Expts</td>
</tr>
<tr>
<td>PBXN-102</td>
<td>40</td>
<td>Slurry — Casting</td>
<td>Mk 80 Series Low Drag Bombs</td>
</tr>
<tr>
<td>PBXC-105</td>
<td>35</td>
<td>Slurry — Casting</td>
<td>Sidewinder</td>
</tr>
<tr>
<td>PBXN-3</td>
<td>33</td>
<td>Slurry — Molding Powd — Pressing — Machining</td>
<td>Continuous — Rod Warhead</td>
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<td>TSE-1002</td>
<td>62</td>
<td>Slurry — Casting</td>
<td>High Expl Simulant</td>
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<td>LX-10-1</td>
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<td>PBXW-106</td>
<td>53b</td>
<td>Slurry — Casting</td>
<td>5”/54 Hi-Frag Proj</td>
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<td>PBXC-303(1)</td>
<td>73</td>
<td>Injection Molding at 12000psi and RT</td>
<td>Booster Expl or Communication Link in FAE, Zuni, Expl Logic Elements, etc</td>
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</table>
Al from 100%, 9.0 ± 0.5%; (6) moisture content by the Karl Fischer method, 0.5% max; (7) compressive strength, by pressing to 30000 psi with subsequent measurement of pellet diam and height to 0.001 inch, 10000 psi min; (8) density, by wt and vol measurement, 1.814 g/cc min; (9) granulation, gravimetrically after w/aerosol OT washing, 100% shall pass thru US Standard Sieve No 4 (4.76 mm), and 2% thru sieve No 200 (74 microns); (10) impact sensitivity, using a 2 kg wt with type 12 tools (NOTS), 50% pt, 16 inches min (≥ HBX-1); (11) vacuum thermal stability, at 120° in 48 hrs using a 5 g sample, 1.0 ml/g max; (12) thermal stability, after exposure for 5 hrs at 135° using methyl violet indicator paper, same color as RDX; (13) moisture stability, by gasometric measurement during a 24 hr exposure to w at 77°, 1.0 ml/g max

PBXN-5. The requirements of the USA military forces are covered by a Mil Spec (Ref 61) which contains the following criteria for Types I and II combs: (1) a production sample which meets specs is required; (2) copolymer consisting of vinylidene fluoride and hexafluoropropylene, by wt difference after digestion with hot 1% NaOH soln and w washing, 5.0 ± 0.5%; (3) HMX (mIL-H-4544Aa) by subtracting the binder percent from 100%, 95.0 ± 0.5%; (4) moisture content by the Karl Fischer method, 0.15% max; (5) granulation, both Type I and II combs, gravimetrically after w/aerosol OT washing – Type I, 99 ± 1% shall pass thru US Standard Sieve No 4 (4.75 mm), Type II, 100%; 60 ± 10% of Type II shall pass thru sieve No 20 (850 microns); 2.5 ± 2.5% of Type I shall pass thru sieve No 40 (240 microns), 1.0 ± 1.0% of Type II; (6) density, by wt and vol measurements, 1.831 g/cc min; (7) impact sensitivity, ERL-Bruceton machine using No 12 tools, 50% pt, 2 kg wt, ≥ Tetryl; (8) vacuum thermal stability at 120° in 48 hrs using a 5 g sample, 0.5 ml/g max; (9) wet bulk density, by wt and vol measurement, 0.80 g/ml min; (10) autoignition temp, by controlled heating of a thermocouple monitored 1 g sample, ≥ 225°; (11) machineability, using a lathe at 158 rpm with w as the coolant, sample shall not crumble or fracture during operation; (12) abrasion resistance, by tumbling 5 pellets in a cardboard box at 20 rpm for 60 min and weighing, wt loss of 2.0% max; (13) workmanship, uniform quality, mfg by standard industrial techniques, and free of foreign materials

a. HMX used for type I shall be grade II, class E; HMX used for type II shall be grade II and consist of 75.0 ± 3.0 parts by wt of class A and 25.0 ± 3.0 parts by wt of class E.

Toxicity. PBXs, per se, are not highly toxic, but careless handling of the expls or their consti
tuents (see Table 2) can cause systemic poisoning by inhalation of dust or vapor, by ingestion, or by contact with the skin

<table>
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<tr>
<th>Constituent</th>
<th>Toxicity</th>
<th>Refs</th>
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<tr>
<td>HNS</td>
<td>Slight</td>
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<tr>
<td>PETN</td>
<td>High, causes headaches, weakness, and a fall in blood pressure; decompn fumes NOx are toxic</td>
<td>86</td>
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<tr>
<td>RDX</td>
<td>Exposure causes epileptiform convulsions; acute oral LD50 for mice is 500 mgs/kg</td>
<td>63, 86</td>
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<td>DOP</td>
<td>Low</td>
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<tr>
<td>Polystyrene</td>
<td>Suspected carcinogen</td>
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<tr>
<td>Teflon</td>
<td>None, except by exposure to pyrolysis or decomp products</td>
<td>86</td>
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Uses. PBX combs are used wherever high mech strength, high energy and excellent heat insensi
itivity are reqd. These requirements encompass such applications as a booster (Refs 8 & 51), a means of connective initiation and logic linkage (Ref 73), a filler in rocket warheads (Gimlet, Sidewinder, Shrike, Zuni, etc; Refs 10, 11, 16, 21, 29, 33, 35 & 38), a bomb filler (Mk 80-
GP-D); Ref 40), a seismic shock generator for the Apollo lunar surface explt package (Refs 55, 60, 65 & 67), a means of metal processing and working (Refs 58 & 69), an expl gas shock wave generator (Ref 59), a simulant for larger ants of expls at great distances (Ref 62), a grenade filler (Ref 53a), the shaped charge in a device for foxhole digging (Ref 45), the filler in the 5"/54 Hi-Frag Proj (Ref 72), and as a filler for the 8" arty fired atomic proj (Ref 74). Additional possible uses are for mil pyrot systs (Ref 75), and as expl fillers for end items such as HEP shells or linear shaped charges which can be used to breach walls or linear shaped charges which can be used to breach walls or urban warfare (Refs 9 & 87)

Listed below in tabular form are the available parameters found for over 43 selected PBX formulations, supported by unclassified refs. Table 3 presents the nomenclature and formulation of each compn; Table 4, sensitivity and stability data; and Table 5, performance parameters.
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<th>1,870.0</th>
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**Selected PEX Type Examples - Composition**

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<tr>
<th>Refs</th>
<th>Density, %</th>
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**Nomencature**

Table 3
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<th>AI, %</th>
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Table 3 – Selected RDX Type Explosives – Composition (continued)


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<th>Notes to Table 4</th>
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<td>a. Small scale test using brass shim spacers</td>
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<table>
<thead>
<tr>
<th>Rms (m/3.84/hr @ 72°C)</th>
<th>Vacuum Stability Test</th>
<th>Impact Test</th>
<th>Impact Sensitivity</th>
<th>Cap Test</th>
<th>Autogasification</th>
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<td>77</td>
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<td>0.013/0.1/0.1</td>
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**Notes:**
- *dB (140 cal/l)*
- *Peak Overpressure, PSI*
- *Impulse, PSI-Mile*
- *Detonation Rate, (H2O/149 cal/l)*
- *M/sec*
Table 5 - PX Type Explosives - Performance Data (continued)

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<th>PX Type</th>
<th>Nominal Pressure, psi</th>
<th>Implant Pressure, psi</th>
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<th>Detonation Rate, ft/sec</th>
<th>O/E, cal/g</th>
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continued...
Written by H. L. HERMAN

Refs: 1) M.B. Frankel et al., "Explosives Research", Aerojet Engrg Corp, Azusa, Calif., Rept No 538, Contract N7onr-46208 (1951)

PCX. Code name for 1,3-Dinitro-1,3,5-triazacyclohexane-5-nitrate

PD. The US military designation for the war gas Phenylidichloroarsine, which is both a blistering agent and a vomiting agent, and has a delayed-action casualty effect (Ref 2). C₆H₅AsCl₂, mw 222.91, colorl liq, bp 252°, fr p -16°, liq d 1.65g/cc at 20°, vap d (compared to air) 7.7

Vapor pressure. 0.021 mm Hg at 20°, 0.113mm Hg at 40°

Volatility. 404mg/m³ at 20°. The vaporizing tendency of PD is too low to give it any value as a blister agent in the field. If dispersed as an aerosol, it would be effective against unprotected troops, although only as an agent with a short duration of effectiveness

Flash point. High enough not to interfere with the mil use of the agent

Decompo temp. Stable to bp

Latent heat of vaporization. 67 cal/g

Rate of hydrolysis. Rapid to HCl and phenylarsenic oxide

Stability in storage. Very stable

Action on metals or other materials. None

Odor. None

Median concon detectable (by nasal and throat irritation). 0.9mg/m³

Median lethal dosage (by inhalation). 2600mg/min/m³

Median incapacitating dosage. 16mg-min/m³ as a vomiting agent; 1800mg-min/m³ as a blistering agent

Skin and eye toxicity. 633mg-min/m³ will produce casualties by eye injury. On bare skin PD is about 90% as blistering as HD (distilled mustard), but it is decompd immediately by wet clothing

Rate of action. Immediate effect on eyes, effects on skin delayed ½ to 1 hr (Ref 1)


PDNA. Abbr for Propylenedinitramine

PE. Abbr for Pentaerythritol (See in this Vol)

PE-1, -2, -3, -3A, -4 Explosives. Brit plastic exps contg RDX, similar in compn to the US Composition C-4 (See Vol 3, C485)

Peak Pressure in Detonation and Explosion.  See Vol 2, B181–2 and Vol 4, D484-R to D485-L

PEAP. Acronym for Pentacyclical Acetate Propionate. See under Pentacyclical Acetate Dipropionate in this Vol

Peat, Nitrated (Nitrotourbe in Fr). When partially dried peat (preferably approaching the lignite stage) is nitrated with nitric-sulfuric acid, tarry expl substances (resembling nitrated tars in appearance) are obtained. If the peat is of recent formation, the nitration reaction proceeds too violently (Ref 1)

Peat has also been used as an ingredient of AN-based blasting expls (Refs 2 & 3)


Pebble Powder (P Powder). See under “P” (Pebble Powder) in this Vol

Pectin Nitrates (Nitropectins). Pectin is a high m n w substance (polyuronide) related to carbohydrates and found in varying quantities in fruits and plants. It consists chiefly of partially methoxylated galacturonic acids joined in long chains. Pectic acid is derived from pectin by treating it with NaOH soin, washing with isopropyl alc, adding alc HCl, and finally washing again with isopropyl alc and drying (Ref 6)

Prior to WWII, attempts were made in Germany to nitrate pectins prepd by extracting sugar beet shavings (Refs 1, 3 & 4). However, the properties of the nitropectins were of no great interest, and they have not found any practical application

Schneider and Ziervogel (Ref 2) obtained nitric esters of pectin as intermediate products which were then esterified by means of acetyl anhydrid to the corresponding acetates. In 1949, Rogovin, Trevys and Shorygina (Ref 5) prep'd pectin nitric esters by nitrating petic acid for 4 hrs at 20° in a mix composed of 48% HNO₃, 50% H₃PO₄ and 2% P₂O₅ to yield a product contg 9.2% N and 7.5% carboxylic groups


Pedersen Device. An invention of the US arms designer J.D. Pedersen, this was a noteworthy ordnance secret of WWI. It consisted of a receiver unit that could be locked into the receiver of a Springfield or Enfield rifle. Installed, it converted the rifle into a semiautomatic weapon that fired .30 cal pistol-type cartridges from a 40-round box magazine. To hide its identity, the mechanism was officially listed as the US .30 cal automatic pistol Model 1918. The system was dropped after the war


Pelargonic Acid Esters. Esters of pelargonic acid or of other open-chain carboxylic acids with 7 to 10 carbon atoms, were claimed by Barsky to be excellent plasticizers in propInits, good muzzle flash reducers without excessive smoke formation, as well as acting to render the propIn compn practically non-hygrosopic. The following are examples of propIn compns containing such esters: 1) NC 86, DNT 10, triethylene-glycol dipelargonate 4%; 2) NC 96, mixed dis- and triethylene glycol pelargonate and caprylate 4%; and 3) NC 82, TNT 15, diethyleneglycol
dihexptaoate 3%

In order to prepare the esters mentioned above, eg, triethyleneglycol dipelargonate, 2 moles of pelargonic acid were heated with 1 mole of triethyleneglycol while bubbling thru a gentle stream of CO₂. During the first 2-3 hours of heating, the temp was raised gradually, to 270°-275°, and maintained for several hours until esterification was complete. The crude product was purified by washing with alkali and water, followed by vacuum drying at 90°. It was then subjected to a bleaching operation with activated C at about 110°, and filtered.

The same procedure was used in the prep of esters of other acids, such as caprylic and heptylic

Barsky also used as a plasticizer, a comprop prepd by heating a mixt of pelargonic acid 80%, caprylic acid 15%, and heptoic acid 5%, with a mixt of diethyleneglycol and triethyleneglycol in equal proportions.

Ref: G. Barsky, USP 2396074 (1946) & CA 40, 3607 (1946)

Paley Explosive Paper (Papier explosible in Fr). See under Explosive Papers or Pyropapers in Vol 6, E424

Pellet Loading. See under Loading and Fabrication of Explosives in Vol 7, L46 to L57

Pellet Powder (Poudre Balle in Fr). BlkPdr compressed into grains of cylindrical shape. It was used by the Brit in large cal cannon before the introduction of “Pebble Powder” (see in this Vol)

Ref: Daniel (1902), 603

Pellet Powder. A special grade of BlkPdr, of approx the same compn as Blasting Powder B (contains NaNO₃ instead of KNO₃), but slightly modified by the addition of various ingredients to control the physical and expl properties. The powder is pressed into cylindrical pellets of approx 2” in length, from 1-1/8 to 2-1/2” in diameter, with perforations 3/8” in diameter. Two to four of these cylinders are wrapped in paraffined paper to form cartridges 4, 6 or 8” in length. They are safer to handle than granular powder, and can be used for various types of blasting, particularly in mining coal, where permissible expts are not required.

Refs: 1) Bebe (1943), 113–114 2) Davis (1943), 49

Pellets, Antiflash. See under Pastilles Antilueurs in this Vol

Pellier Explosive. A Fr expl invented in 1884 contg K perchlorate 67.1, K nitrate 8.4, sulfur 8.4, fine sawdust 6.0, and extract of campeachy weed 10.1%

Ref: Daniel (1902), 603

Pellier Résine Explosive. A Fr expl invented in 1886, with a brownish color, resembling a resin in appearance. It was prepd by the nitration of sugar with mixed nitric-sulfuric acids.

Ref: Daniel (1902), 603

Pelouze, Théophile-Jules (1807–1867). Fr scientist who made many important contributions to organic and inorganic chemistry. He nitrated paper in 1838, and was thus probably the first to prepare NC. Pelouze did not recognize the importance of his work, and thought that his product was identical with nitrated starch (which he called “xyloïdine”), prepd in 1833 by Bacroon (see Vol 2, B259-R). Much better grade NC was prepd in 1846, independently by Schönhchin and Bottger, by the nitration of cotton.

Ref: Davis (1943), 245–8

Pembrite. A Brit mining expl contg AN 93–96, vegetable oil 3–6, sulfur 1–2 and Ba nitrate 1%

Ref: Daniel (1902), 604

Pendulum, Ballistic, Test. See under Physical Tests in Vol 1, VII to VIII (Also see A. Schmidt, Explosivst 1962, 23-34)
Pendulum Chronographs. (Pendelchronographs in Ger). A mechanical-electrical device to measure the velocity of a projectile in flight. Cranz (Ref, p79) describes the Navez-Leurs chronograph used in Fr for several years beginning in 1853, until replaced by the LeBoulengeChronograph in 1866 (see Vol 3, C307-R to C308-R). Another pendulum chronograph was invented by Casperson (Ref, p129).

Note: Pendulum chronographs are not the same as ballistic pendulum chronographs (see Vol 2, B6-R).

Ref: Cranz 3 (1927), 79 & 129

Pendulum, Friction, Apparatus. See under Friction Sensitivity Tests in Vol 6, F204-L to F206-L.

Penetration Aids (Pen Aid). Generic name for devices and tactics intended to assist the penetration of aircraft and missiles against defense systems. Six main classes of Pen Aid have been prospected: 1) use of chaff, jamming or nuclear blackout to hide delivery vehicles or warheads from defense radars; 2) the saturation of defense radars by the use of multiple warheads (including MIRV payloads), and target simulations such as decoys, balloons or false radar echoes; 3) the shielding of missile warheads against weapon effects, and the use of maneuverable re-entry vehicles; 4) active defense against interceptors by means of anti-ABM missiles or anti-SAM missiles in strategic bombers, and 5) salvage fusing — this is intended to detonate the offensive weapons, and especially ICBM warheads when interception appears probable, or, more practically, upon sensing the first effects of interceptor weapon effects. This reduces the effectiveness of the offense since its weapon is still not on target, but it may achieve a partial kill.

A further evasion measure specifically intended against ballistic-missile defenses is a low trajectory flight pattern for strategic missiles. This reduces the height and therefore the radar visibility of incoming warheads, thus complicating the defense’s mission.


Penryn Antifrost Powder (or Antifrost Penryn Powder). A Brit expi which passed the Buxton Test (see Vol 2, B394-R). It contained a nitrated mixt of glycerin and ethylene glycol 9, AN 60, woodmeal 9, and Na chloride 22%. Power by BalPend 2.42" (vs 3.27" for standard Brit Gelignite contg 60% NG).

Ref: Marshall 3 (1932), 120

Penta. One of the names for Pentaerythritol Tetranitrate (PETN) (See in this Vol)

Pentaborane. See Vol 2, B254-L to B256-R


3-Pentadecylphenol. HO.C6H4(CH2)4CH3 mw 304.52. Can be prep’d by a series of reactions from cardanol, HO.C6H4.C14.H27, obtained by distg cashew-nutshell liq at reduced press, or by steam distn at atm press (Ref 1).

Trinitro-3-pentadecylphenol. (O3N)3(HO)C6.H.C15.H31, mw 439.57, N 3.19%, mp 89–90° (impure 82–86°). Can be prep’d by nitration of 3-pentadecylphenol, as described in BritP 627928 (Ref 2). It is an expl compd


PENTAERYTHRITOL AND ITS DERIVATIVES

Pentaerythritol [Pentaerythrite, Tetraakis(hydroxymethyl)methane, Tetramethylolmethane, Methanetetramethylole, 2,2-Bis(hydroxymethyl)-1,3-propanediol (name
Currently preferred by CA), Pentek, Penetol, Pentamethylthritol (Ger), Pentamethylenetritol (Russ), PE1, C(CH2OH)4,
C5H12O4, mw 136.15, white tetragonal crystals (frequently twinned), mp 262–3°C (crystl grades mp 180–250°C (Refs 1 & 18). By using resublimed PE a mp of 265.5°C was obtained from the mp curve (Ref 10). A phase change at 187.7°C from the tetragonal to the cubic system was also found. The Q of transition and fusion were found to be 10.5 and 1.7-kcal/mole resp (Ref 10). Its bp is 270°C at 30mm with sublim (Refs 5 & 12); d by flotation of a single cryst is 1.39g/cc (Ref 6); RI 1.548 (Ref 18); CA Registry No 115-77-5

Historical. PE was first isolated by Tollens who was examining the effect of heat and reagents on formaldehyde. Apparently the crude formaldehyde he was working with contained a small % of acetaldehyde, which accounts for the PE formed. Although Tollens isolated it in 1882, it was not identified as PE until 1888 (Ref 2). Further details of the prepn and props of PE appeared in 1891 (Ref 3). The prepn is essentially a condensation betw 3 moles of formaldehyde and 1 of acetaldehyde to give an intermediate tris(hydroxymethyl)acetaldehyde which is not isolated. An intermolecular oxidn/redn then takes place betw this intermediate, and a 4th mole of formaldehyde, giving PE and formalic ac (Ref 13, p 2). This type reaction is discussed under Cannizaro Reaction in the Encycl (Vol 2, C25).

Preparation. Its prepn on a lab scale is given in Ref 7. A detailed exp tl proc for its prepn on a cmol (1000 lb) scale is given in Ref 4 as follows: In the reactor is placed 3175 lb of 37% formaldehyde and ca 700 lb of w. To this is added with stirring 1050 lbs of 50% NaOH at a rate so as to keep the temp at 15–20°C (with cooling if necessary). Then is added 285 lbs of 99% acetaldehyde under the surface of the soln with vigorous stirring and cooling so as to keep the temp at 20–5°C. The mixt is held at 25–30°C for several hours and then held at 60°C until the acetaldehyde concn falls to 0.1%. The mixt is transferred to a neutralizing tank where formic ac is added until the pH is 7.8–8.0. The soln is transferred to an evaporator, evapd to a d of 1.27g/cc, chilled, and the crude PE filtered off using a wringer or a Nutsche filter. The crude PE, yield 85–90% based on acetaldehyde, conts poly(pentaerythritols) (see Encycl Vol 5, D1407) plus small amts of pentaerythritol ethers and cyclic formals. It is suitable for mfg resins, plastics, and drying oils; but can be further purified as follows: the crude cake is dissolved in dil aq HCl, activated C added, the soln filtered hot, chilled, and the crystals filtered. By evapn of the filtrate and chilling 2nd and 3rd crops may be obtained. The mother liquors and filtrates may be recycled to recover Na formate and poly(pentaerythritols). A variation of the process uses lime as the condensing agent instead of NaOH. In this case the soln is neutralized with sulfuric ac instead of formic ac, the pptd Ca sulfate filtered, the filtrate treated with oxalic ac to ppt the remaining Ca ions, and the PE isolated as above (Ref 4).

A flow sheet of this process is in Ref 16. PE can be sepd from the last traces of the dimer and higher polymers by prepn of the cyclic dibenzylidene deriv which is recrystd from hot acet, mp 164.5°C (Ref 13, p 154). The latter is hydrolyzed with aq HCl in a continuous app which can be scaled up to the kg scale (Ref 8).

Analysis. Quant detn with Ce(IV), proc: a sample contg 3–16mg of PE is mixed with a 50–100% excess of the Ce(IV) reagent, 1 ml of catalyst B and 8.5ml 72% perchloric ac added, the mixt heated on a hot plate at 95°C until a pink color develops, the mixt quenched by chilling, 10–15ml of 6M sulfuric ac added, and the excess Ce(IV) back titrated with std Fe(II) soln. For prep of reagents and calcs see Ref 15.

Reactions. PE readily forms esters with organic and inorganic acids (Refs 9, p 157 & 13, pp 54, 212 & 246); and cyclic as well as open chain acetals and ketals (Refs 9, p 195 & 13, p 141). Some of these prods are used in expls, while others
give valuable expls on nitration. For info on individual cmpds of interest see below under Derivatives of PE

**Solubility** (g/100g solv) w 6.5 at 25°, 90 at 100°; EtOH 0.5 at 25°; glycerol 10.3 at 100°; diethylene glycol 7.7 at 100°; formamide 21.3 at 100°; sl sol in dioxane, pyridine, and liq ammonia; insol acet, bz, C tetrachloride, eth, oils, fats, & petr eth (Ref 12)

**Specification.** US Armed Forces requirements for PE intended for mfg of PETN are given in US Army Mil Spec MIL-P-20304 (1951) as follows: *Color*—white; *Moisture*—max 0.5%; *Melting Point*—min 250°; *Hydroxyl Value*—min 49.0%; *Water Insoluble*—max 0.25%; *Chloride*—max 0.01%; *Ash*—max 0.10%; and *Granulation*—through US No 18 sieve, min 100%; through US No 20 sieve, min 99%; and retained on US No 100 sieve, min 90% **Thermal Decomposition.** In the presence of Al oxide PE at 270–80° was found to give Me alc, CO₂, w, & 2-methylacrolein. In the presence of powd Cu bronze less Me alc and more 2-methylacrolein were formed (Ref 10)

**Toxicity.** Low, the finely divided dust is a nuisance hazard (Ref 19)

**Uses.** Its primary use in peacetime is for the prep of esters, ethers, ketals, etc., which have widespread use in the paint, plastic, and resin indus (Ref 9). In WWII, PE esters of long chain unsatd fatty acids were developed as a substitute for tung oil, whose supply from China was cut off (Ref 13, p 231). In wartime large quants are consumed in the mfg of PETN, Petrin, and other nitrate esters (see below). A castable expl has been patented contg 12.66% of a 49/51% Na nitrate/Mg di- nitrate euteqt, 50.65% AN, 11.68% PE, and 25% Hexogen (Ref 14). Mixts of PE with powd metals (Al, Mg, and alloys of these) react to form metal oxides, C, and H. The reaction is very exothermic (Q_{reaction} 1.49–1.55 kcal/g) and the mixts are readily ignited. Other props: crit diam for complete comb 21 mm, burning rate 31 x 10^{5}g/cm² sec (Ref 17)

*Written by* C. H. Mc Donnell


**Pentaerythritol Mononitrate** [2,2-Bis(hydroxymethyl)-1,3-propanediol 1-mononitrate (name preferred by CA), PEMN]. C₅H₁₁NO₆₃, mw 181.15, N 7.73%, crysts from chlf, mp 79° (Ref 2), CA Registry No 1607-00-7

Best prep is by melting together a mixt of PE tetrakis(trifluoroacetate), PE, and K carbonate for 1 hour, extn of the cooled and powd melt with methyl chloride, treatment of the ext with 99% nitric ac, and working up to give a PE nitrate/trifluoroacetate mixt. This mixt is hydrolyzed with MeOH/K carbonate and the hydrolysate sep'd by fractionation between eth & w to give a 40% yield of the pure mononitrate (Ref 3)

Pentaerythritol Mononitrate (Tris[tris(di-fluoromethyl)methyl] ether), FA-PEMON.
C₈H₁₈F₃N₂O₆, mw 682.19, N 20.52%, OB to CO₂ +2.35%; a shock sens. liq.
CH₂OC(NF₂)₃
O₂NCH₂CH₂OC(NF₂)₃
CH₂OC(NF₂)₃
Prepd by the addn of perfluoroguanidine to PFEN followed by fluorination of the adduct. Procedures for the prepn of this type compd are described in Refs 3, 4 & 5 Explosive Properties. Qf −158kcal/mole, Qe 1599cal/g; impact sensy PA app 5.1cm (PETN 30cm); iricn sensy measured as girt hardness for expln 4 (PETN above 9) (Ref 2)

Written by C. H. McDONELL


Pentaerythritol Dinitrate [2,2-Bis(hydroxymethyl)-1,3-propanediol, 1,3-dinitrate (name preferred by CA), PEDN].
C₈H₁₈N₂O₆, mw 226.15, N 12.39%, OB to CO₂ −49.6%; a liq, bp 150° at 10mm; d 1.476g/cc at 20/4°, RI 1.4928 at 20° (Ref 4), CA Registry No 1607-01-8

It has been prepd by the action of Ag nitrate on PE dibromide, yield 92% (Ref 2); by the same procedure as used for the prepn of the mononitrate (see above) (Ref 4); and by the nitration of the mono-benzylidene deriv of PE followed by hydrolysis of the benzylidene group (Ref 5). It is one prod which has been isolated by thin layer chromatography from the hydrolysis of PETN (Ref 3). The IR spectrum is in Ref 2, p 11; and the impact sensy by the BM app is 100cm (PETN 17cm) (Ref 2). It has been patented as a plasticizer for NC (Ref 5)


Pentaerythritol Cyclic Ether Dinitrate [Oxy-pentaerythritol Dinitrate, 3,3-Bis(nitratomethyl)oxetane (name preferred by CA)]. C₈H₁₈N₂O₇, mw 208.13, N 13.46%,

\[
\text{H}_2\text{C} \quad \text{O} \quad \text{CH}_2
\]

OB to CO₂ −49.6%; a solid, mp 89–91° (Ref 4); cryst d 1.76g/cc (Ref 3). It is prepd by the action of Na ethoxide on Petrin (Ref 4), or by the action of di-N pentoxide in chlf on oxetane-3,3-dimethanol (Ref 6); Qe 851cal/g (Ref 2). There is a differential thermal analysis exotherm at 160° (Ref 5). The impact sensy is similar to RDX and Tetryl and the ign temp is 233° (Ref 3)

Pentaerythritol Dicarbonate Dinitrate.
C₆H₁₄N₂O₁₀, mw 310.22, N 9.03%, OB to CO₂ −77.4%; a solid, mp 47° (Ref 4). It is prepared by acetylation of Pentaerythritol Dinitrate (Ref 4). Its impact sens is with a 2kg wt is 175cm for no explns (PA 35cm) (Ref 3). It has been patented as an ingredient in expls, proplnts, and ign devices (Ref 2)


Pentaerythritol Diallyl Ether Dinitrate.
C₁₇H₃₈N₂O₇, mw 366.27, N 9.15%, OB to CO₂ −120.3%; a liq, d 1.191g/cc at 20°, RI 1.4688 at 20°. Other physical and expl props are given in Ref 2


Pentaerythritol Dichloride Dinitrate [2,2-Bis(chloromethyl)-1,3-propanediol Dinitrate (name preferred by CA)].
C₅H₆Cl₂N₂O₆, mw 263.04, N 10.65%.
CH₂Cl
O₂NOCH₂CH₂ONO₂
CH₂Cl
A mixt with PE monochlorohydrydtritrinitrate (see below), mp 43–50°, gives a Pb block expansion of 107% of TNT and is less shock sens than TNT

Refs: 1) Beil, not found 2) Urbanski 2 (1965), 192

Pentaerythritol Bis(tris(difluoramino)methyl Ether) Dinitrate, FA-PEDIN.
C₇H₁₄F₁₂N₈O₈, mw 560.17, N 20.0%, OB to CO₂ −11.4%; a shock sens liq. Prepd
CH₂OC(NF₂)₃
O₂NOCH₂CH₂ONO₂
CH₂OC(NF₂)₃
by the addn of perfluoroguanidine to PEDN followed by fluorination of the adduct (for refs to the prepn of this type compd see under Pentaerythritol Mononitrate, FA-PEMON)

Explosive Properties. Q₉ −147kcal/mole; Q₈ 1582cal/g; impact sens on PA app is 5cm (NG 10cm), on Bruceton app 2.3cm (NG 10cm)


Pentaerythritol Diformate Dinitrate.
C₇H₁₀N₂O₈, mw 282.17, N 9.93%, OB to CO₂ −83.1%. Its impact sens with a 2kg wt is 175cm for no explns (PA 35cm) (Ref 3). It has been patented as an ingredient in expls, proplnts, and ign devices (Ref 2)

Refs: 1) Beil, not found 2) Westfälische-Anhaltische Sprengstoff A-G, GerP 638432-3 (1936) & CA 31, 1212(1937) 3) Blatt, OSRD 2014 (found on Class of Compounds page “Nitrates”)

Pentaerythritol Dimethyl Ether Dinitrate.
C₇H₁₄N₂O₈, mw 254.20, N 11.02%, OB to CO₂ −81.9%; a solid, mp 53–4° (Ref 3); impact sens with 2kg wt, no explns at limit of machine (Ref 3); power by Pb block expansion 97% of PA, 106% of TNT (Ref 3). It has been patented for use in expls, proplnts, and ign devices (Ref 2)

Written by C.H. McDonnell


Pentaerythritol Trinitrate (Petrin).
HOCH₂C(CH₂ONO₂)₃, mw 271.1, N 15.48%; OB to CO₂ −26.6%. Production grade material is a viscous liq (mp <20°). Purified Petrin melts at 26–28°. It decomps (without boiling) at 130° and 4mm Hg. At 20° its d is 1.54g/cc.
The viscosity of production grade material is as follows:

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<th>Temp (°C)</th>
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</table>

(Ref 15). The vapor press of Petrin at 60° is 4.5 x 10⁴ mm Hg (Ref 13). The dipole moment of Petrin is 5.06D (Ref 5a).

Petrin is used in the preparation of Petrin-acrylate which is a monoproplnt that can also be used as a high energy polymerizable binder (Ref 15). Petrin is also an intermediate in the prepn of many mixed nitrate esters (Refs 3 & 7). Dallet claims Petrin as a constituent of proplnt binder compn (Ref 8), and Crescenzo et al. (Ref 9) claim it as a plasticizer for slow-burning proplnt compns. Its use in a binder for cloud-seeding pyrotechnic compns is claimed by Finnegan & Burkard (Ref 11). Foltyn et al. state that it is an excellent gelling agent for NC (Ref 13). Such gels are claimed to be stable between -20 and +50°. Petrin is used in medicine as a vasodilator (Ref 7).

An analytical method based on its IR absorption at 5.82 microns has been developed by Rohm & Haas (Ref 4). A thin-layer chromatographic sepn and identification of a Petrin (as well as other impurities) in PETN was recently developed by Yasuda (Ref 14). He used Nasulfanilate-impregnated Zn dust-silica gel G plates which he developed with an acet-benz solvent. The spots thus produced were diazotized and identified photometrically.

Preparation. A number of prepn methods for Petrin have been reported in the open literature. The first of these (at least the first that is well-documented) is that of Marans et al. (Ref 2) in which pentaerythritol (PE) monocotate is reacted with 100% nitric acid at 0° to give PE acetate trinitrate. After recrystallizing the latter from hot ethanol it is treated with a 10% NaOH-water soln to produce a viscous oil which is recryst from water to give Petrin. A more economical method was then also developed by ABL (Ref 3). This improved method utilized direct nitration of PE, at 0°, by a mixed acid consisting of 80% nitric acid and 20% sulfuric acid. The product, prepresenting a mixt of PETN with trinitrate, is ppted by adding water.

To separate the components the acet soln, neutralized by means of ammonium carbonate, is treated with aq alc so as to form a mixt of 7 parts of acet, 3 parts of water, and 2 parts of ethanol. PETN pptts from this soln, while Petrin remains in the liquor to be completely sepd as a ppt by further treatment with hot water. The yield of trinitrate amounts to about 50%.

A further improvement involves the essentially simultaneous synthesis and extrn of Petrin from the reaction mixt. Methylene chloride solvent is added to the PE/nitric acid mixt before the addition of sulfuric acid. After adding the sulfuric acid the solvent is removed, and fresh solvent is added and removed several times. The combined solvent extracts are neutralized and concd. Yields of 60 to 65% are claimed (Ref 15).

A somewhat similar technique was patented by Brown (Ref 6) who removed Petrin or nitric acid from the equilibrium reaction mixt. Petrin was removed by reacting it with a carboxylic acid, and nitric acid was removed by reacting it with benz or phenol.

A method which appears to be essentially equivalent to the best ABL method was patented by Brennecke (Ref 10) who claims better utilization of the spent acid and solvent and better yield in a repetitive, step-wise procedure. Another modification patented by Rolewicz et al. (Ref 12) utilizes mixed acid and methylene chloride extrn and appears to be little different from the above methods, except that the nitric acid is made oxide-free. A method of obtaining 98.4% pure Petrin from its mixts with PETN and PE dinitrate is claimed by Brennecke (Ref 16).

Chemical properties. As already stated, Petrin is an intermediate in the prepn of numerous mixed esters. Marans et al. (Ref 2) prepd a series of Petrin-nitrobenzoate esters by reacting Petrin with the appropriate nitrobenzyol chloride. They also prepd Petrin-formate, acetate, propionate, oxalate, glutarate, succinate, adipate, and phthalate. An especially important Petrin derivative is Petrin-acrylate. It is prepared by reacting Petrin with a mixt of acrylyl chloride and dimethylaniline (Ref 4).

Explosive Properties. Relatively little information has been published on the expl props of
Petrin. The earliest reference to its prep'n and use appears to be in German patents (Ref 1). Ref 15 gives its heat of explosion as 1204cal/g, and its impact sensitivity as 5 to 10 inches on the PicArn impact machine (or roughly equivalent to Tetryl).

The writer (Ref 8a) detd explosion times of Petrin rapidly heated in small stainless steel tubes (Wenograd test). The measurement scatter was too large to obtain reliable kinetic data. It was possible, however, to establish an approx. minimum explosion temp. of about 280° under these test conditions. For comparison, the Wenograd test results gave minimum explosion temps of about 420° and about 280° for TNT and NG respectively.

Written by J. ROTH


Pentarythritol Tetranitrate (PETN; listed as 1,3-Propanediol, 2-2-[bis(nitroxy)methyl]-dinitrate in CA since 1972, Penta; Penthrate in Fr; Pentitr, Niperyth, Nitropenta (NP) in Ger; TEN in Russ). C(CH₂ONO₂)₄, mw 316.15, N 17.71%, OB to CO₂ -10.1%. Color: tetragonal crystals of 1.77g/cc d, melting at 141–42° (pure), and having a RI=1.558. An orthorhombic crystal modification has a d of 1.72g/cc (Ref 92).

An enormous amount of material has been published on PETN. There are some 360 CA references since 1961! The older literature is also very voluminous (see Additional Refs).

Consequently, the writer has chosen to emphasize modern work in this article, of course including important older studies. The article is divided into the following sections: 1. Physical Properties; II. Solubility; III. Chemical Properties; IV. Specifications and Analytical; V. Uses; VI. Preparation; VII. Detonation Characteristics; VIII. Thermal Decomposition; IX. Combustion & DDT (delegation-to-detonation transition); X. References. The major emphasis will be placed on Sections VII, VIII and IX.

1. Physical Properties

Vapor Pressure. The vapor pressure, p (in cm Hg) of solid PETN is given by Edwards (Ref 14) as log p = 16.73 - 7750/T where T is the absolute temp. The vapor press of liq PETN, according to Crimmings (Ref 73), is log p = 14.44 - 6352/T where p is in mm Hg. Earlier vapor press measurements by Belyaev (Ref 10) appear to be too high because of PETN decom. Crimmings data give a heat of vaporization of 29.0 kcal/mole as compared to 23 kcal/mole obtained by Belyaev. Edwards' heat of sublimation is 36.3 kcal/mole. Then, by difference with the Crimmings heat of vaporization, the heat of fusion of PETN is about 7 kcal/mole. However, recent studies by Rogers & Vinegar (Ref 90) show that the heat of fusion of single crystals of PETN is 11.8 kcal/mole and may be as low as 9.8 kcal/mole due to surface imperfections.

Thermochemical and thermal characteristics. Standard heat of formation: 128.7 kcal/mole (Ref 74a). Specific heat: 0.272cal/deg g at 115° (Ref 8); 0.24 cal/deg g at 25° (quoted in Ref 94). Coefficient of heat conduction: 6 x 10⁻⁴ cgs units (Ref 19). Linear coefficient of thermal...
Fig 1  Linear coefficients of PETN (Ref 91)

expansion: average over 88°C (above room temp)  
11 x 10^{-5} \text{cm/cm°C} for 1.6g/cc PETN aggregates  
(Ref 60). See Fig 1 for Cady's data (Ref 91)  
for single crystal PETN  

Electrical Properties  
Packing density (g/cc)  

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>Dielectric Constant (at 30GHz, Ref 92)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>2.45</td>
</tr>
<tr>
<td>1.5</td>
<td>2.58</td>
</tr>
<tr>
<td>1.6</td>
<td>2.73</td>
</tr>
<tr>
<td>1.7</td>
<td>2.89</td>
</tr>
<tr>
<td>1.75</td>
<td>2.95 at 25GHz</td>
</tr>
</tbody>
</table>

Dipole moment: 4.74D (Ref 27)  

Optical & Spectral Properties. Mullen & Orloff  
(Ref 100) give the uv absorption spectra of  
PETN in MeCN soln from 1825 to 3900Å.  
Bands exist at about 1935, 2600 & 2900Å.  

Molecular orbital calcs assign these bands to  
the following transitions:  \( \pi \rightarrow \pi^* \) localized on  
NO\(_2\) for the 1935Å band;  \( n \rightarrow \pi^* \) transition of  
the NO\(_2\) group for the 2600 & 2900Å bands  

Galeev et al (Ref 71) used lasers to obtain  
light reflectivity of PETN. At 6943Å & 10600Å  
they obtained reflectivities of 0.79 & 0.81,  
respectively. Roth (Ref 46) measured the dif-  
fuse reflectivity of PETN aggregates of varying  
packing density, particle size & particle shape.  
He found that packing density and particle size have little effect on reflectivity. Particle  

shape appears to have some effect, in that  
needle-shaped particles are somewhat poorer  
reflectors than other shapes. Diffuse reflectivity  
varyes between about 0.9 and 1.0 in the visible,  
and starts to decrease rapidly below 3500Å.  
Some approx absorptivity measurements suggest  
that absorptivity of PETN aggregates varies  
exponentially with the aggregate density, \( \rho \), its  
thickness, \( h \), and wavelength. Approx absorp-  
tion coefficients, \( \alpha \), corrected for reflectivity,  
are shown below as a function of wavelength, \( \lambda \)  

\[
\begin{array}{c|c}
\lambda (\text{Å}) & \alpha (\text{cm}^2/\text{g})^* \\
2800 & \sim 2100 \\
2900 & \sim 1700 \\
3000 & 1300 \\
3100 & 1000 \\
3500 & 550 \\
4000 & 420 \\
\end{array}
\]

* from \( \frac{1}{t_{\text{inc}} - t_{\text{refl}}} = \exp (-\alpha \chi) \) for \( \phi \leq 4 \text{mg/cm}^2 \)  
The absorption of a single crystal of PETN  
as measured by Deb (Ref 19) is shown in Fig 2  

Field ionization and electron impact ionization  
mass spectra are given by Bruneel et al (Ref 54)  
Mechanical Properties & Sound Velocity. Hoge  
(Ref 77) obtained the following ultimate stress  
as a function of strain rate for machined discs  
(1.77g/cc) of PETN (all failures were brittle  
fractures)  

Fig 2  Absorption spectrum of a single crystal of  
PETN [Deb, according to Bowden & Yoffe  
(Ref 19)]
Strain rate (sec^{-1}) & Ultimate stress (psi) 
\hline
10^3 & 160 \\
10^2 & 215 \\
10^1 & 215 \\
1.0 \times 10^3 & 720 \\
1.12 \times 10^3 & 700 \\
1.3 \times 10^3 & 785 \\
2.6 \times 10^3 & 840 \\
\hline

Cramer (Ref 17) gives the bulk modulus for 1.77g/cc PETN as 4.6 \times 10^{10} dyne/cm^2.

An important mechanical property of an expl is its behavior under shock loading. This behavior can be described by its shock Hugoniot (or simply Hugoniot) as discussed in Vol 7, H179-L. For expl aggregates (not single crystals), establishing a Hugoniot presents both conceptual and expl difficulties. However, even an approx Hugoniot can be useful in many applications.

In the following tabulation we show Hugoniots for PETN aggregates at various densities. The Hugoniots are in the linearized form of \( U = a + bu \) where \( U \) is the shock velocity, \( u \) is the particle velocity, and \( a \) and \( b \) are constants.

From the data of Holland et al (Ref 18a) and Campbell et al (Ref 28) one obtains \( U = 5.56 \) mm/\( \mu \) sec and \( u = 1.14 \) mm/\( \mu \) sec for single crystal PETN (\( \rho = 1.77 \) g/cc). Use of the constants for \( \rho = 1.72 \) g/cc (Ref 79) in the above tabulation gives \( u = 1.08 \) mm/\( \mu \) sec for \( U = 5.56 \) mm/\( \mu \) sec in reasonable, though possibly fortuitous, agreement with the single crystal results.

Recently Bauer (Ref 107) has proposed a method of generating \( P-u \) (shock pressure–particle velocity) relationships (non-reactive Hugoniots) for any packing density \( \rho \) from the known \( P_1-u_1 \) relationship at some density, \( \rho_1 \). His equations are:

\[
u^2 = u_1^2 + \frac{P}{2\rho_{\text{cryst}}} \left( \frac{P}{1-p} \right) \quad (1)
\]

and

\[
u_1^2 = \frac{a(b)}{b} \left[ 1 + \frac{2P}{\rho_{\text{cryst}} a^2} - \sqrt{1 + \frac{4P}{\rho_{\text{cryst}} a^2}} \right]
\]

\[
\frac{P}{2\rho_{\text{cryst}}} \left( \frac{P_1}{1-p_1} \right) \quad (2)
\]

where \( a \) and \( b \) are the constants in the linearized form of the Hugoniot (see above), \( \rho_{\text{cryst}} \) is the crystal density of the material, and \( p = 1 - \rho/\rho_{\text{cryst}} \) and \( p_1 = 1 - \rho_1/\rho_{\text{cryst}} \) are porosities.

Sound velocities for PETN pressings are shown in the tabulation on the following page. The writer (Ref 60) found precursor compressive waves in PETN aggregates shocked up to 10kbar.

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>Temp (°C)</th>
<th>( a ) (mm/( \mu ) sec)</th>
<th>( b ) (dimensionless)</th>
<th>Experimental range of ( u ) (mm/( \mu ) sec)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88</td>
<td>25</td>
<td>0.47</td>
<td>1.73</td>
<td>0.76–3.50</td>
<td>75</td>
</tr>
<tr>
<td>1.0</td>
<td>25</td>
<td>0.76*</td>
<td>0.66*</td>
<td>0.28–0.42</td>
<td>26</td>
</tr>
<tr>
<td>1.59</td>
<td>25</td>
<td>1.33</td>
<td>2.18</td>
<td>0.03–0.37</td>
<td>74 (p 222)</td>
</tr>
<tr>
<td>1.60</td>
<td>25</td>
<td>1.32</td>
<td>2.58</td>
<td>0.2 –0.5</td>
<td>79</td>
</tr>
<tr>
<td>1.72</td>
<td>25</td>
<td>1.83</td>
<td>3.45</td>
<td>0.2 –0.6</td>
<td>79</td>
</tr>
<tr>
<td>1.72</td>
<td>25</td>
<td>2.33</td>
<td>2.34</td>
<td>0.2 –0.6</td>
<td>94</td>
</tr>
<tr>
<td>\textit{\gamma}1.55</td>
<td>110</td>
<td>\textit{\gamma}0.6*</td>
<td>8.7*</td>
<td>0.24–0.29</td>
<td>74 (p 222)</td>
</tr>
</tbody>
</table>

* Very approximate
<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>Longitudinal (mm/µsec)</th>
<th>Bulk (mm/µsec)</th>
<th>Precursor (mm/µsec)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.77</td>
<td>—</td>
<td>2.42</td>
<td>—</td>
<td>75</td>
</tr>
<tr>
<td>1.72</td>
<td>2.933</td>
<td>2.326</td>
<td>—</td>
<td>94</td>
</tr>
<tr>
<td>1.67</td>
<td>2.8</td>
<td>—</td>
<td>—</td>
<td>74, p 358</td>
</tr>
<tr>
<td>1.59</td>
<td>2.6</td>
<td>—</td>
<td>2.45</td>
<td>60</td>
</tr>
<tr>
<td>1.59</td>
<td>2.4</td>
<td>—</td>
<td>—</td>
<td>74, p 358</td>
</tr>
<tr>
<td>1.55 (a)</td>
<td>—</td>
<td>—</td>
<td>2.25 (a)</td>
<td>60</td>
</tr>
<tr>
<td>1.54</td>
<td>1.8</td>
<td>—</td>
<td>—</td>
<td>74, p 358</td>
</tr>
<tr>
<td>1.48</td>
<td>1.7</td>
<td>—</td>
<td>—</td>
<td>74, p 358</td>
</tr>
</tbody>
</table>

(a) Heated to 110°C

**Interatomic Distances.** According to Booth & Llewellyn (Ref 9) the interatomic distances in PETN are: 1.50Å for C–C; 1.37Å for C–O; 1.36Å for O–N; 1.27Å for N–O (nitro)

**Packing Density.** The following tabulation of packing density as a function of loading press is given by Urbański (Ref 44, p 180)

<table>
<thead>
<tr>
<th>Pressure, kg/cm²</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>351</td>
<td>1.575</td>
</tr>
<tr>
<td>703</td>
<td>1.638</td>
</tr>
<tr>
<td>1406</td>
<td>1.710</td>
</tr>
<tr>
<td>2109</td>
<td>1.725</td>
</tr>
<tr>
<td>2812</td>
<td>1.740</td>
</tr>
</tbody>
</table>

**II. Solubility**

PETN is insoluble in water but is soluble in a variety of organic solvents and particularly in acetone. This is clearly shown in Table 1 which contains the data of Urbański & Kwiatkowski (Ref 3), and in Table 2 which shows the more recent results of Roberts and Dinegar (Ref 21)

---

**Table 1**

**Solubility of Pentaerythritol Tetranitrate in Organic Solvents (Ref 3)**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>PETN (g) dissolved in 100g of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Alcohol</td>
<td>Ether</td>
</tr>
<tr>
<td>0</td>
<td>0.070</td>
</tr>
<tr>
<td>10</td>
<td>0.085</td>
</tr>
<tr>
<td>20</td>
<td>0.115</td>
</tr>
<tr>
<td>30</td>
<td>0.275</td>
</tr>
<tr>
<td>40</td>
<td>—</td>
</tr>
<tr>
<td>40</td>
<td>0.415</td>
</tr>
<tr>
<td>50</td>
<td>0.705</td>
</tr>
<tr>
<td>60</td>
<td>1.205</td>
</tr>
<tr>
<td>62</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>2.225</td>
</tr>
<tr>
<td>78.4</td>
<td>3.795</td>
</tr>
<tr>
<td>80.2</td>
<td>—</td>
</tr>
<tr>
<td>90</td>
<td>—</td>
</tr>
<tr>
<td>113</td>
<td>—</td>
</tr>
</tbody>
</table>
Table 2
Solubility of Pentaerythritol Tetranitrate (Ref 21)
Grams/100 Grams of Solvent

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Acetone</th>
<th>Benzene</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>20.81</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>20</td>
<td>24.84</td>
<td>0.275</td>
<td>0.125</td>
</tr>
<tr>
<td>25</td>
<td>30.56</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>30</td>
<td>34.56</td>
<td>0.496</td>
<td>0.213</td>
</tr>
<tr>
<td>40</td>
<td>44.92</td>
<td>0.834</td>
<td>0.378</td>
</tr>
<tr>
<td>50</td>
<td>58.76</td>
<td>1.448</td>
<td>0.657</td>
</tr>
<tr>
<td>60</td>
<td>—</td>
<td>2.389</td>
<td>1.196</td>
</tr>
</tbody>
</table>

The solubility of PETN in acetone-water mixtures was determined by Aubertain (Ref 11) and is shown in Table 3. These data are of great importance in industrial practice.

Values of PETN solubility in ethyl acetate and pyridine, as reported by Desvergnes (Ref 5) are given in Table 4:

Table 4
Solubility of Pentaerythritol Tetranitrate
[Desvergnes (Ref 5)]

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>PETN (g) dissolved in 100g of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>19</td>
<td>6.322</td>
</tr>
<tr>
<td>50</td>
<td>17.868</td>
</tr>
</tbody>
</table>

Other solubility data from various sources quoted in AMCP 706-177 are shown on the following page:

Table 3
Solubility of Pentaerythritol Tetranitrate in Acetone-Water Mixtures
[Aubertain (Ref 11)]

<table>
<thead>
<tr>
<th>Amount of PETN dissolved in 100g of solvent g</th>
<th>Acetone concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55%</td>
</tr>
<tr>
<td>Temperature of solution, °C</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>52</td>
</tr>
<tr>
<td>2.5</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>17.5</td>
<td>—</td>
</tr>
<tr>
<td>20</td>
<td>—</td>
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<td>25</td>
<td>—</td>
</tr>
<tr>
<td>30</td>
<td>—</td>
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<td>35</td>
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<tr>
<td>45</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>—</td>
</tr>
<tr>
<td>55</td>
<td>—</td>
</tr>
<tr>
<td>60</td>
<td>—</td>
</tr>
</tbody>
</table>
Solubility, grams of PETN per 100 grams (%): of:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Trichlorethylene (or Alcohol)</th>
<th>Acetone</th>
<th>Benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>%</td>
<td>°C</td>
<td>%</td>
<td>°C</td>
</tr>
<tr>
<td>0</td>
<td>0.070</td>
<td>0</td>
<td>14.37</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0.195</td>
<td>20</td>
<td>24.95</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>0.415</td>
<td>40</td>
<td>30.56</td>
<td>40</td>
</tr>
<tr>
<td>60</td>
<td>1.205</td>
<td>60</td>
<td>42.68</td>
<td>80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Methyl acetate</th>
<th>Ether</th>
<th>β-Ethoxy-ethyl-acetate</th>
<th>Chlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>%</td>
<td>°C</td>
<td>%</td>
<td>°C</td>
</tr>
<tr>
<td>20</td>
<td>13</td>
<td>0</td>
<td>0.200</td>
<td>20</td>
</tr>
<tr>
<td>30</td>
<td>17</td>
<td>20</td>
<td>0.340</td>
<td>30</td>
</tr>
<tr>
<td>40</td>
<td>22</td>
<td>34.7</td>
<td>0.450</td>
<td>40</td>
</tr>
<tr>
<td>50</td>
<td>31</td>
<td></td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
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<th>Temperature</th>
<th>Ethylenedichloride</th>
<th>Methanol</th>
<th>Tetrachloroethane</th>
<th>Carbon tetrachloride</th>
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</thead>
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<td>%</td>
<td>°C</td>
<td>%</td>
<td>°C</td>
</tr>
<tr>
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<td>50</td>
<td>2.6</td>
<td>60</td>
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</tbody>
</table>

Dimethylformamide is also a good solvent for PETN. According to Lang (Ref 15a): at 40°C 100g of soln contain 40g PETN. at 60°C 100g of soln contain 50g PETN at 100°C 100g of soln contain 70g PETN. PETN forms eutectics with a number of liq or molten nitro-aromatic compds. The compns and melting points of some of these as reported by Urbański (Ref 4) are:

\[
\text{mp (°C)} = \frac{20° \times 100g}{20g} + 40° \text{for Toluene}
\]

20% PETN with 80% m-dinitrobenzene 82.4
10% PETN with 90% 2,4-dinitrotoluene 67.3
13% PETN with 87% o-nitrotolueno 76.1
30% PETN with 70% Tetryl 111.3
20% PETN with 80% Mannitol 101.3

Hexanitrate
PETN forms a eutectic with NG which contains 98.5% NG and melts at 12.3° (Ref 6).

A diagram of the PETN-TNT system is shown under Pentalites in this Vol

Unlike other nitrate esters, PETN does not form a colloid soln with NC.
Solubilities of PETN in 60-95% nitric acid in the temp range of 0-50° were determined by Camera & Mauro (Ref 63), and in 20-100% nitric acid at 23-25° by Aubertin (Ref 11).

Nearly equi-dimensional PETN crystals rather than the usual needle-like crystals can be obtained by slow cooling of a 40% soln of PETN in boiling EtOAc (Ref 12).

The prepn of large single crystals of PETN (and other expls) is described by Koch (Ref 98)

III. Chemical Properties
Due to its symmetrical structure, Pentaerythritol Tetranitrate is highly resistant to many reagents. Thus PETN differs from the majority of nitrate esters by not being readily decomposed by sodium sulfide at 50°. On the other hand, it is decomposed quite quickly by boiling in a ferrous
chloride soln. Boiling with a 2.5% soln of NaOH causes very slow decomp, whereas NC rapidly decomp under these conditions

Aubertin & Rehling (Ref 15) have shown that treatment with water at approx 100°C causes PETN to hydrolyze. At 125°C and under pressure, hydrolysis proceeds quite quickly, and is considerably enhanced by the presence of 0.1% HNO₃. Regardless of whether it occurs in water alone or in water acidified with nitric acid, the hydrolysis produces mainly Pentachloroerythritol Dinitrate. A dil NaOH soln causes PETN to hydrolyze more rapidly than acidified water. PETN neither reduces Fehling's reagent nor enters into addition products with any aromatic nitro compd. In this respect it differs from both Erythritol Tetranitrate and Nitromannitol

Hydrolysis of PETN in concd nitric acid solns was studied by Camera & Mauro (Ref 63)

Urbanski et al (Ref 7) found that the addition of mono-, di- and trinitro derivatives of benz or toluene to PETN lowers its thermal stability as detd by heating the mixt in the temp range 120-132°C. The extent of thermal decomp of PETN, heated alone or in mixts, can be estimated by the decreasing pH which indicates formation of acidic decomp products. Fig 3 shows how the addition of TNT enhances PETN decomp

The authors suggest that the deleterious effect of nitro compds is due to the lowering of the mp of these mixts as compared to pure PETN, and a faster decomp in the liq than in the solid phase. A more detailed examination of PETN decomp will be found in Section VIII

According to AMCP 706-177, the compatibility of PETN with metals is:

Dry: Copper, brass, aluminum, magnesium, magnesium-aluminum alloy, stainless steel, mild steel, mild steel coated with acid-proof black paint and mild steel plated with copper, cadmium, nickel or zinc are not affected

Wet: Stainless steel is unaffected and aluminum only very slightly so after prolonged storage. Copper, brass, magnesium, magnesium-aluminum alloy, mild steel, mild steel coated with acid-proof black paint and mild steel plated with cadmium, copper, nickel or zinc are affected

IV. Specifications & Analytical

According to the “Requirements” of MIL-P-387A (9 Jan 1957) as modified by EOPA-50352-2 (1 Nov 1967) & MIL-P-387B (7 Nov 1967), PETN for USA military use shall conform to:

Melting Point. The melting point of PETN shall be 141 degrees Centigrade (°C) plus or minus 1.0°C

Nitrogen Content. The nitrogen content of PETN shall be 17.50 percent minimum (min) Acetone insoluble material. The acetone insoluble material of PETN shall be 0.10 percent maximum

Insoluble particle. There shall be no evidence of insoluble particles in PETN

Acidity or Alkalinity. The acidity or alkalinity shall not exceed 0.01 percent max

120°C vacuum stability. The maximum amount of gas evolved in 20 hours test time shall be 5 milliliters

Granulation. The PETN shall comply with the granulation requirements shown below, except that the granulation requirements for Class 3 PETN shall not apply to PETN used in coprecipitated pentolite

Granulation Requirements:

<table>
<thead>
<tr>
<th>US Std</th>
<th>Percent Passing</th>
<th>Specified Sieve</th>
</tr>
</thead>
<tbody>
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<td>Class 2</td>
</tr>
<tr>
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<td>100 min</td>
</tr>
<tr>
<td>80</td>
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<td></td>
</tr>
<tr>
<td>100</td>
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<td>96 min</td>
</tr>
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<td>140</td>
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<td>200</td>
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<td>80 max</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>65 min</td>
</tr>
</tbody>
</table>
Superfine PETN for use in EBW detonators and MDF is produced by quenching a hot acetone soln in cold water. The resulting particle size distribution averages 10 microns, and irregular crystals are produced which are easier to initiate (Ref 80a).

The prescribed analytical method for determining nitrogen content in PETN is the MIL-STD-286 Method 209.3. The ferrous chloride-titanous chloride method described for NG in Vol 6, G106-7 is also applicable to PETN.

A method of analysis based on converting nitrate groups to ammonia with Devarda's alloy is described by Smeenk (Ref 103). PETN is dissolved in ethanol and the ammonia formed is titrated with standard acid soln.

In recent years, a number of thin-layer chromatographic methods for the qual detection of PETN have appeared in the literature. Hennig (Ref 51) used glass plates, chl solvent, and a diphenylamine soln in coned sulfuric acid as the color developer. He experienced difficulty in distinguishing between PETN and NG. The method of Boehm (Ref 53) is similar to that of Hennig except that Boehm uses a silica gel G column and a mixt of pet-ether and EtOAc as solvent. Barnes (Ref 58) used silica gel G-H2O plates, CCl4-acet solvent, and diphenylamine dissolved in acet/alc as color reagent. Parther et al (Ref 57) use Mg silicate and Al2O3 plates, various solvents and the Griess-Romijn color reagent. Vich et al (Ref 78) compare the effectiveness of various chromatographic methods for separating and identifying nitrate esters.

Fredricks & Pristera (Ref 23) describe an IR method for determining small amounts of D-pentaerythritol tetranitrate (see Vol 5, D1410-13) in PETN.

Hetman (Ref 102) describes polarographic methods for analyzing explosives (including PETN).

V. Uses

The principal uses of PETN are in the expl core of industrial detonating fuses (eg Primacord of MDF - mild detonating fuse), and in the base charge of commercial blasting caps. It is also used as the entire expl charge in exploding-bridgewire (EBW) detonators (see Vol 6, E353-R). In military applications PETN has been largely replaced by RDX due to the latter's better thermal stability and shelf-life. Some PETN is still needed to make Pentolites (see Pentolite in this Vol) which are used as expl charges in hand grenades. A recent patent (Ref 97) claims caseless grenades and other munitions made of PETN & Al cast into a thermostetting resin. Pentolite and PETN/plastic binders are used in commercial boosters for insensitive commercial expls such as ANFO, or insensitive slurry explosives. PETN is also used in medicine as a vasodilator.

In recent years PETN sheet explosive, consisting of PETN in a rubber-like elastic matrix, has found considerable use in metal-forming, metal-cladding and metal-hardening. Physical & expl characteristics of rubber-bonded sheet expl are described by W. Kegler & R. Schall (Ref 45, p 496), by Kegler (Ref 59), and in Refs 30c, 65a and 105a. The prep and resulting physical properties of PETN-Epikote 871 (an epoxy resin) sheets is described by Sato (Ref 49). Extrudable, putty-like comps, consisting of 80/20 PETN/silicone rubber, capable of detonation in small diameter are described by Sherman & Vigneault (Ref 83), and Ref 91a.

Low-detonation pressure composites consisting of PETN (and other expls) in a low-density (foam) plastic matrix (eg polyurethanes) are described by Abegg et al (Ref 33).

Numerous patents have been issued on PETN-plastic comps usually in the form of sheet expl. Some of these are briefly summarized below.

Brez & Davis (Ref 29) claim a compn consisting of 92.5-70 parts of PETN and 7.5-30 parts of binding agent containing 25-75% of an organic rubber and 75-25% of a thermoplastic terpene resin. The product may be rolled or pressed to any desired shape. Noddin (Ref 55) claims a sheet expl based on PETN bound with Teflon. Williams (Ref 101) claims a detonating cord composed of an extrudable compn containing 60-85% PETN/10-40% polyethacrylate rubber /0-10% plasticizer.

Some specialized uses of PETN are summarized below. Expendable cartridges for small arms are made by coating unglazed grains or single base smokeless powder with PETN, spraying with plasticized thermoplastic binder and compression molding to the desired shape (Ref 99). Tucker et al (Ref 85) describe a spark detonator without primary expls. Secondary
expl, spark detonators have useful commercial applications because of their low cost, and because the detonators as well as the firing sets are safe. The firing set must be closely coupled to the detonator if minor firing energies are to be realized. Spark detonators loaded with PETN can be fired with stored energies of 10–60 mJ if the firing circuit is capable of delivering most of its energy in a sufficiently short period of time. Spark initiation of secondary expls depends on both the amount and the rate of energy expended in the spark gap.

A novel use of PETN or rather PETN detonation products in high stagnation temp lasers is claimed by Robinson (Ref 95). These N₂–CO₂ and N₂–CO gas lasers are based on expl products obtained from detonation of mixts of PETN and acrylonitrile, or detonation of PETN in O₂ or O₂/He mixts.

VI. Preparation

PETN was first prepared in 1894 by the nitration of pentaerythritol, PE (Ref 1). This is still the basic method used today. Commercial production of PETN could not be realized until the formaldehyde and acetalddehyde required in the synthesis of PE became readily available about a decade before WWII.

Basically, most processes for the commercial production of PETN involve pouring PE into 98+% nitric acid (sp gr 1.50–1.52g/cc) at a temp not exceeding 25°. Since PETN is only slightly sol in nitric acid it ppt's near the end of the nitration. The ppt is then filtered, washed with water, "neutralized" with Na₂CO₃ soln, and recrystd from acet. In some processes the nitric acid is diluted with water after nitration. This is believed to keep some of the impurities in soln.

Details of a number of manufacturing methods are given by Urbanski (Ref 44, pp 185–91). These methods are rather similar. For example, a semi-continuous method used in Germany during WWII had the following material balance per 100kg of PETN: "44.4kg of PE and 224kg of nitric acid (98–99%), of which 80kg enter into the reaction, 16kg are lost, 128kg are recovered as 30% nitric acid, and resulted in 96.8% yield."

A process for making heat-stabilized PETN, claimed by Voigt (Ref 56), involves dissolving PETN and a stabilizer such as polyvinylpyrrolidinone in a solvent such as N-methyl-2-pyrrolidinone, and pptg the stabilized PETN by slowly pouring the above soln into rapidly stirred water or ethanol. The PETN thus made is claimed to meet military stability requirements.

The general mechanism of nitrating alcohols to form nitrate esters is described under Nitration in this Vol. Several specific remarks about PETN are contained in that article. The industrial nitration of PE differs from most nitrate esters in that it employs concd nitric acid rather than mixed acid. Nevertheless nitration via the nitronium ion mechanism, which is the preferred mechanism in mixed acid nitrations, is also feasible in concd nitric acid. However, Eremenko and co-workers claim that the nitrating agent in PE nitrations, in mixed acid, is "ionized" nitric acid (Refs 39 & 76). The present writer does not find Eremenko's arguments to be very convincing. In any case, commercial production of PETN employs nitric acid and not the mixed acids of Eremenko's studies.

VII. Detonation Characteristics

In general terms, PETN can be characterized as a "sensitive", brisant, and powerful high expl. Explosive sensitivity is a rather nebulous quantity, but there can be no doubt that PETN is a much more "sensitive" material than TNT, but rather less sensitive than Lead Azide. In particular, PETN requires very little priming charge (less than 1 mg LA) to initiate its detonation. This is the characteristic that makes PETN so widely used in blasting cap base charges, in detonating cord and in boosters.

Brisance and "power" are quantities that can be defined more exactly than sensitivity, and PETN is one of the most powerful and brisant expls known. It is also among the most studied expls, from both expl and theoretical points of view. In this section we will consider PETN's steady detonation parameters, thermochemistry, and initiation characteristics, including theoretical models for various types of initiation.

A. Steady Detonation Parameters

Undoubtedly the most frequently and accurately determined detonation parameter of any expl is its detonation velocity, D. This is certainly true for PETN. Detonation velocity varies with packing density, ρ, charge diameter, d,
charge confinement, and expl particle size. Some results of the many published studies of D vs \( \rho \) are shown in Tables 5 and 6. As shown in Table 7, the expression, obtained by H.C. Hornig et al (Ref 74, pp 503–512),
\[
D = 3.19 + 3.7(\rho - 0.37), \text{ in mm/sec} \tag{1}
\]
provides a good fit to the data (particularly the data of Table 5) over the entire measurement range, although it is claimed (Ref 74) that it is valid over \( 0.37 \leq \rho \leq 1.65 \text{g/cc} \).

The same reference gives
\[
D = 7.92 + 3.05(\rho - 1.65) \text{ for } \rho \geq 1.65 \text{g/cc} \tag{2}
\]
\[
D = 2.14 + 2.84\rho \text{ for } \rho \leq 0.37 \text{g/cc} \tag{3}
\]
Cook (Ref 18) gives:
\[
D = 5550 + 3950(\rho - 1.00) \text{ in m/sec. This expression fits the data for } 0.5 \leq \rho \leq 1.5 \text{g/cc reasonably well, but gives D lower than observed for } \rho < 0.5 \text{g/cc, and higher than observed for } \rho > 1.5 \text{g/cc.}
\]

### Table 5

**PETN Experimental Detonation Velocities**
(Ref 74)

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>Detonation Velocity (mm/\mu sec)</th>
<th>Density (g/cc)</th>
<th>Detonation Velocity (mm/\mu sec)</th>
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<tr>
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</tr>
<tr>
<td>1.765</td>
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</tr>
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<td>5.83†</td>
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</tr>
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<td>0.241</td>
<td>2.81*</td>
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</tr>
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<td>7.49†</td>
<td>0.185</td>
<td>2.67†</td>
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<table>
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<tr>
<th>Shock Electric Effect Measurement†</th>
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</tr>
<tr>
<td>1.44</td>
</tr>
<tr>
<td>1.38</td>
</tr>
</tbody>
</table>

* Unconfined rate stick
† Cylinder test
‡ All other data are detonation pressure expts

There are few quant data for D vs d for PETN. However, it is certain that the diameter effect for PETN is quite small. This becomes apparent when one considers that the critical diameter for PETN (at \( \rho = 1 \text{ g/cc} \) and 0.025–0.1 mm particle size) is only 0.9mm (Bobelev quoted in Ref 22, p 348), and becomes smaller at \( \rho > 1 \). Cook et al (Ref 18) show that D varies from about 4800m/sec at d=0.32cm to 5400 m/sec at d=1.6cm, for -65 to +100 mesh PETN at 0.95g/cc. Since confinement effects parallel diameter effects, D for PETN is almost independent of confinement for any practical size charges.

Fairly large variation in PETN particle size has relatively little effect on D (this writer, unpublished results, 1949). Cook et al (Ref 18) show that there is an interaction between particle size and diameter effects. At comparable packing densities of 0.95g/cc, PETN of -35 to +48 mesh and PETN of -65 to +100 mesh detonate at about 4500 and 4800m/sec respectively at a charge diameter of 0.32cm, whereas at charge diameters of 0.63cm and larger there is no difference in D for the two particle size fractions.

Stesik (Ref 81) measured D for PETN/Al and PETN/Be mixts.

By depositing low concns of PETN on foamed polystyrene, Archibald (Ref 47A) obtained very low density expl systems. At an apparent PETN density of 0.09g/cc he found D = 2.05 mm/\mu sec. D could be varied by changing the PETN concn.

### Table 6

**PETN Experimental Detonation Velocities**
(Various Sources)

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>Detonation Velocity (mm/\mu sec)</th>
<th>Refs</th>
<th>Density (g/cc)</th>
<th>Detonation Velocity (mm/\mu sec)</th>
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### Table 7
PETN Experimental Detonation Pressures
(Ref 74)

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<tr>
<th>Density (g/cc)</th>
<th>Dimensions of PETN Diameter x Length (inches)</th>
<th>Fitted Detonation Velocity (mm/μsec) (Eqs 1,2,3)</th>
<th>Detonation Pressure $P_{CJ}$ (kbar)</th>
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<td>Shock Electric Effect Measurements</td>
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<td>208</td>
</tr>
<tr>
<td>1.44</td>
<td>1 x 1</td>
<td>7.14</td>
<td>199</td>
</tr>
<tr>
<td>1.38</td>
<td>1 x 1</td>
<td>6.91</td>
<td>173</td>
</tr>
<tr>
<td>1.23</td>
<td>1 x 1</td>
<td>6.38</td>
<td>136</td>
</tr>
<tr>
<td>1.23</td>
<td>1 x 1</td>
<td>6.37</td>
<td>134</td>
</tr>
<tr>
<td>1.23</td>
<td>1 x 1</td>
<td>6.37</td>
<td>137</td>
</tr>
<tr>
<td>1.23</td>
<td>1 x 1</td>
<td>6.37</td>
<td>142</td>
</tr>
<tr>
<td>1.23</td>
<td>1 x 1</td>
<td>6.36</td>
<td>141</td>
</tr>
<tr>
<td>0.99</td>
<td>1 x 0.5</td>
<td>5.48</td>
<td>87</td>
</tr>
<tr>
<td>0.95</td>
<td>1 x 0.5</td>
<td>5.33</td>
<td>85</td>
</tr>
<tr>
<td>0.93</td>
<td>1 x 1.5</td>
<td>5.27</td>
<td>73</td>
</tr>
<tr>
<td>0.93</td>
<td>1 x 1</td>
<td>5.26</td>
<td>77</td>
</tr>
<tr>
<td>0.93</td>
<td>1 x 1.5</td>
<td>5.25</td>
<td>70</td>
</tr>
<tr>
<td>0.89</td>
<td>1 x 1</td>
<td>5.10</td>
<td>71</td>
</tr>
<tr>
<td>0.88</td>
<td>1 x 1</td>
<td>5.06</td>
<td>68</td>
</tr>
</tbody>
</table>

| Optical (Smear Camera) Measurements |
| Density (g/cc) | Dimensions of PETN Diameter x Length (inches) | Fitted Detonation Velocity (mm/μsec) (Eqs 1,2,3) | Detonation Pressure $P_{CJ}$ (kbar) |
| 0.48 | 1.5 x 1 | 3.60 | 24 |
| 0.30 | 1.5 x 0.5 | 2.99 | 24 |
| 0.29 | 1.5 x 1 | 2.96 | 15 |
| 0.27 | 1.5 x 0.5 | 2.91 | 5 |

| Quartz Crystal Measurements |
| Density (g/cc) | Dimensions of PETN Diameter x Length (inches) | Fitted Detonation Velocity (mm/μsec) (Eqs 1,2,3) | Detonation Pressure $P_{CJ}$ (kbar) |
| 0.25 | 1.75 x 1 | 2.83 | 8 |
| 0.25 | 1.75 x 1 | 2.83 | 7 |
| 0.25 | 1.75 x 1.5 | 2.83 | 6 |

The PETN Detonation Pressure, $P$ (also called the CJ Pressure), is shown as a function of packing density in Table 7 and in Fig 4. Note that the measured $P$ values in Fig 4 lie quite close to the theoretical curve developed by Lee & Hornig (Ref 72), which is based on a Wilkin's type equation of state (see Vol 4, D294-L) with a Gruneisen ratio, $\Gamma$, for the detonation products, that is solely a function of specific volume. Shea et al obtained an effective $\Gamma = 8.077 p - 12.288$ (Ref 74).

However, on p 511 of Ref 74, Mader shows that the BKW equation of state (see Vol 4, D272) fits the extpl PETN pressure data just as well (compare Figs 5 and 4).

Zubarev & Teglin (Ref 40a) developed an equation of state for detonation products based on the dynamic compressibility data for these substances and the requirement that product volume be minimized. For PETN they compute the following:

<table>
<thead>
<tr>
<th>$\phi$ (g/cc)</th>
<th>$D$ (m/sec)</th>
<th>$P$ (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5700</td>
<td>88</td>
</tr>
<tr>
<td>1.25</td>
<td>6720</td>
<td>150</td>
</tr>
<tr>
<td>1.67</td>
<td>8160</td>
<td>270</td>
</tr>
<tr>
<td>1.77</td>
<td>8610</td>
<td>310</td>
</tr>
</tbody>
</table>
Fig 4  PETN Detonation Pressure vs Density (Ref 74, p 508)

Note that these values are fairly close to those shown in Table 7 and Figs 4 and 5, as well as the expn and computed D – ρ data for Fig 6 (Hornig et al, Ref 74) and Fig 7 (Mader, Ref 74). Thus it is abundantly clear that comparison of expn and computed D and/or P data provides no real test of the validity of an equation of state of detonation products, since P and D data computed on the basis of widely different equations of state can be made to agree with measured P and D values.

A much more rigorous test of the validity of a detonation product’s equation of state is provided by the comparison of observed and computed detonation temps (CJ temps), T_{CJ} and/or detonation product compns which depend on T_{CJ} and to a lesser extent on P. Unfortunately, there are no expn detonation product compns, and expn T_{CJ}’s are open to serious uncertainties, particularly so in the case of solid expls. For example, Blackburn and Seely (Ref 48) in studying the light produced by the detonation of PETN, of varying degree of compaction and varying particle size, found that light intensity was not affected by the nature or even the presence of interstitial gases. For large particles,
It is obvious that the calculated $T_{CJ}$ depends strongly on the equation of state used in the computation. Unfortunately, as already stated, there are no unequivocal expls $T_{CJ}$'s for PETN (and probably not for any expl) to compare theory and expt. However, note that for all three equations of state cited above, $T_{CJ}$ increases as $\rho_0$ decreases.

We will not list $u_p$ or $V$, the steady detonation particle velocity and detonation product specific volume, as they are completely determined by the conservation equations, namely:

$$u_p = \frac{P}{\rho_0} D$$

$$V = \frac{1}{\rho_0} \left(1 - u_p/D\right)$$

and can be computed from the listed $P$ and $D$ values of Table 7, etc.

Compns of PETN detonation products and the heat of detonation will be discussed in the next subsection.

Kury et al. (Ref 45, p 3) made accurate measurements of the fragment velocity of expl-filled copper cylinders. Based on the kinetic energy of the fragments, they were able to obtain a relative energy scale (ie, a measure of the efficiency of various expls in propelling metal fragments) for several expls. On this scale Comp B grade A is chosen as a standard and assigned a value of 1.00. Other common expls have the following relative energies:

- HMX 1.30
- PETN 1.21
- TNT 0.74
- NM 0.56

Initial velocities of explosively driven metal fragments can be accurately estimated by the so-called Gurney formula (see Vol 6, C195-R). The writer (Ref 81a) used the Ref 45 data referred to above to compute a Gurney constant $\sqrt{2E'}$ (for tangential detonation) of 3.04mm/\usec for 1.765g/cc PETN.

AMCP 706-177 (1971) gives the power of PETN as 145% of TNT in the Ballistic Mortar and 173% of TNT in the Trazul block. It also lists PETN's braise at 1.5g/cc as 129% of TNT as ddet in plate dent test. The Russians use a somewhat different measure of power which they call "total efficiency". This involves computing expln product expansion to 1 atm. Andreev & Belyaev (Ref 25, p 655) list the "total efficiency" of 1.6g/cc PETN at 134% of TNT.
PETN is an effective underwater expl. Its shockwave energy and bubble energy relative to Pentolite (see in this Vol) are 1.15 and 1.13, respectively (Ref 21a).

Because PETN sheet expl (PETN/elastomer in sheet form) has assumed such importance in a variety of expl applications, we now present some of its detonation parameters.

Detonation velocity of sheets containing 15% natural rubber is given in Figs 8 & 9 as functions of sheet thickness and density. These data are taken from Kegler & Schali (Ref 45, p 499), who show that the decrease in D produced by stretching the sheet is due to a decrease in sheet density.

Jones (Ref 88, p 125) gives $D = 7.0 \text{mm/\mu sec}$ and $P = 184\text{kbar}$ for Dupont Datasheet C (63% PETN, 8% NC, 29% elastomers).

Another Dupont sheet explosive is EL506D. It contains about 70% PETN and has a density of 1.4g/cc. Gurney constants for it are 2.50mm/\mu sec (Roth, Ref 81a) and 2.28mm/\mu sec (Kennedy, Ref 88, p 117).

XTX-8003, an extrudable expl, contains 80% PETN and 20% silicone rubber at a nominal density of 1.55g/cc (its theoretical max density is 1.556g/cc). At around its nominal density, $D = 7.3\text{mm/\mu sec}$ and $P = 170\text{kbar}$. Its heat of detonation is 1.16kcal/g (Ref 92).

B. Thermochemistry. Ornellas (Ref 52a) obtained some very accurate measurements of the heat of reaction and reaction product compn of PETN decmpd in an inert atm, for both highly confined and unconfined PETN samples. His results are shown in Table 8. Also included in this table are computed decmpn products calc'd under the assumption that the product gases are ideal and at equil at 1600°K and 1 atm.

It is clear from these data that neither $\Delta H$ nor the major products for PETN are affected by sample confinement. It is most interesting that measured product compn and $\Delta H$'s match closely the computed ideal gas equil compn for $T = 1600°K$ and 1 atm. This implies that as the products expand and cool, equil is frozen at around 1600°K, i.e., reaction rates become so slow below 1600°K that the product compn remains essentially unchanged upon further product expansion and cooling.

Under CJ conditions, where pressures are extremely high, the so-called soot reactions

- $\text{CO} + \text{H}_2 = \text{C}_5 + \text{H}_2\text{O}$
- $2\text{CO} = \text{C}_5 + \text{CO}_2$

should favor formation of free carbon and depletion of CO. Of course, for an expl that is oxygen balanced or nearly so, there is little CO or H$_2$ in the products under most conditions. It seems that Lee & Hornig (Ref 72) chose to ignore the soot reactions and they write

$$\text{C}_5\text{H}_8\text{N}_4\text{O}_{12} = 4\text{H}_2\text{O} + 3\text{CO}_2 + 2\text{CO} + 2\text{N}_2$$
Table 8
PETN Decomposition*
(according to Ornellas, Ref 52a)

<table>
<thead>
<tr>
<th></th>
<th>Confined Sample</th>
<th>Unconfined Sample</th>
<th>Computed**</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^***$ kcal/g</td>
<td>1.49</td>
<td>1.50</td>
<td>1.52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product Composition (moles/mole PETN)</th>
<th>Confined Sample</th>
<th>Unconfined Sample</th>
<th>Computed**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>3.39</td>
<td>3.50</td>
<td>3.50</td>
</tr>
<tr>
<td>CO</td>
<td>1.64</td>
<td>1.59</td>
<td>1.50</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.003</td>
<td>&lt; 0.0002</td>
<td>none</td>
</tr>
<tr>
<td>C$_s$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3.50</td>
<td>3.45</td>
<td>3.50</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.45</td>
<td>0.51</td>
<td>0.50</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.037</td>
<td>&lt; 0.0002</td>
<td>1.5 x 10$^{-5}$</td>
</tr>
<tr>
<td>HCN</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

* $\rho_0 = 1.74g/cc$

** Ideal gas equilibrium at 1600$^\circ$K and 1 atm

*** (H$_2$O)$_q$

for the CJ reaction. This leads to a heat of detonation, Q, of 1.38kcal/g

Mader (Ref 40), on the other hand, did take the soot reactions into account and he obtains the following CJ products (minor products ignored):

C$_5$H$_8$N$_4$O$_{12}$ =

3.95CO$_2$ + 0.96CO + 0.95C$_s$ + 4.00H$_2$O + 2N$_2$

at $\rho_0 = 1.77g/cc$

3.89CO$_2$ + 0.22CO + 0.88C$_s$ + 4.00H$_2$O + 2N$_2$

at $\rho_0 = 1.67g/cc$

3.04CO$_2$ + 1.96CO + 3.96H$_2$O + 0.025H$_2$ + 2N$_2$

and minor amounts of CH$_4$, NH$_3$ & NO

at $\rho_0 = 1.2g/cc$

3.04CO$_2$ + 1.96CO + 3.94H$_2$O + 0.050H$_2$ + 1.99N$_2$ + 0.02NO

and minor amounts of NH$_3$, H, OH & CH$_4$

at $\rho_0 = 1.0g/cc$

The Q's for these reactions are respectively 1.51, 1.50, 1.38 and 1.38kcal/g

Measurements of the electrical conductance of PETN detonation products, obtained by Hayes (Ref 45, p 599) show that conductance increases with PETN packing density. Since the peak conductivities of PETN, NM, Comp B and liq TNT appear to be a linear function of the free carbon content of their respective detonation products (as calculated by Mader, Ref 40), Hayes justifiably claims that the amount of free carbon in detonation products controls the conductivity of such products. If so, the dependence of PETN detonation product conductance on initial PETN density favors Mader's detonation product computations since, as shown above, Mader calculates that the amount of free carbon decreases with a decrease in PETN packing density.

The product comps measured by Ornellas (Table 8) and the Mader CJ compositions differ appreciably. The Q's are, however, very similar. The agreement between calorimeter and computed Q's is certainly unexpected in view of the different product comps. Nevertheless, as stated in Vol 7, H38-39, there is rather good agreement between calorimeter Q's for confined samples and the CJ Q's computed by Mader (Ref 40) for expls that are not too deficient in oxygen. The following tabulation illustrates this:
<table>
<thead>
<tr>
<th>Material</th>
<th>Q_{\text{exp}} (kcal/g)</th>
<th>Q_{\text{comput}} (kcal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN</td>
<td>1.49</td>
<td>1.51</td>
</tr>
<tr>
<td>HMX</td>
<td>1.48</td>
<td>1.48</td>
</tr>
<tr>
<td>RDX</td>
<td>1.51</td>
<td>1.48</td>
</tr>
<tr>
<td>9404</td>
<td>1.41</td>
<td>1.38</td>
</tr>
<tr>
<td>LX-04</td>
<td>1.31</td>
<td>1.31</td>
</tr>
<tr>
<td>NM</td>
<td>1.23</td>
<td>1.30</td>
</tr>
<tr>
<td>TNT</td>
<td>1.09</td>
<td>1.27</td>
</tr>
</tbody>
</table>

Note that disagreement between expl and computed values increases as the oxygen deficiency of the expl increases.

Olenko & Parshov (Ref 48b) determined that the ratio of PETN underwater shockwave energy to Q is 0.77 at $\rho_0 = 1.6\text{g/cc}$ and 0.47 at $\rho_0 = 0.7\text{g/cc}$.

**Initiation Characteristics.** Usually the initiation characteristics of an expl are examined from two different points of view, namely, how to obtain reliable initiation, and how to avoid accidental initiation. It is the latter point of view that we will emphasize, since, as stated at the beginning of this section, there is no problem in initiating PETN reliably. Conversely, PETN, because of its “sensitivity,” is prone to accidental initiation. We will now proceed with the description of various modes of initiation of PETN. For general modes of expl initiation see Vol 7, 1106–109.

**Initiation by exploding bridge.** This subject has been studied extensively by Leopold (Refs 32a, 41 & 43). He used a smear camera to observe the growth of expl in PETN, and a condenser discharge to explode the bridge wire. He found that the diameter of the wire can be chosen so as to favor time reproducibility of expln, reliability of detonation, or vigor of the bridge-wire output. To cause detonation, there is an optimum length for each wire material, apparently governed by the energy density in the wire, and a minimum critical volume of expl that must be initiated. No single parameter was found to be correlated with the ability of the wire to effect detonation over a wide range of parameters. Beneficial trends, however, are readily apparent. These include a high-power input producing high temps and pressure; a sustained electrical energy input just after the wire bursts to provide simultaneous electrical and chemical energy contributions during the critical growth to the detonation period; vigorous wire explns to ensure ignition of a definite critical volume of expl, and use of wire materials with low bp and heats of vaporization for greater heat transfer (Ref 41).

In a subsequent study (Ref 43), Al, Au, Pt, and W wires were investigated to determine the effect of the wire material on the initiation of PETN by exploding wires. The wires were exploded by a 1-uf capacitor charged to 2000v. The results indicate that favorable wire materials are those into which energy is deposited at a rapid rate. They also have low bp’s and heats of vaporization. Heat of oxidation of the wire material plays only a minor role. Different wire materials have different optimum lengths for effecting detonation.

Blackburn & Reithel (Ref 42) also studied the initiation of PETN by exploding bridge wires using smear camera techniques. Photographs thru the transparent head of a detonator revealed that the shock wave generated by the exploding wire accelerates until it becomes a detonation wave in the expl. The rate of this evolution is increased by increasing the sp surface of the granular expl and by increasing the intensity of the bridgewire expln. Initiation was studied by pressing PETN into a transparent container against a bridgewire. Photographs of the initiation to detonation of the expl were taken both by the self-light of the process, and by external illumination from a second exploding wire.

**Initiation by Electrostatic Discharge.** Jackson (quoted in Vol B, E45) found the max non-ignition voltage and non-ignition energy for 2.6\(\mu\) PETN to be 12000v and 0.036 joules at 500MMF capacitance and a spark gap of 0.005 inches. Previous investigations (also quoted in the above Ref) showed max non-ignition energies of 0.062 and 0.085 joules for PETN of unspecified (but probably larger than 2.6\(\mu\)) particle size. Circuit parameters for these tests were also not specified in Vol B. In any event, PETN handling is not a particularly hazardous operation from the static discharge point of view.

Recently Romanov and Sten'gach (Ref 89) found that discharge energies for 50% expls of PETN increased with: PETN particle size, packing density, water content, circuit inductance, and a decrease in ambient temp. The discharge energy-inter electrode distance curve
passes thru a minimum. They claim that shock waves have a significant role in the discharge initiation process.

Initiation by flame and heat will be described in sections VIII and IX.

Impact and Friction Initiation of PETN have been extensively studied. This general subject is summarized in Bowden & Yoffe (Refs 13 & 19), Afanas'ev & Bobolev (Ref 85a), and Vol 7, I35-55, which contains a rather complete description of impact initiation with many refs to the impact and friction initiation of PETN. There is general agreement that impact and friction initiation proceed via a hot spot mechanism (see Vol 7, H170-75). There is, however, considerable doubt and controversy about the mechanisms of hot spot formation.

As discussed in Vol 7, it is rather futile to assign numerical values to the impact or friction sensitivity of PETN (or any other expl), although the average critical stress of ~5kbar for PETN impact initiation (Ref 85a) may be significant. It is significant, however, that in most, and probably all, relative rankings of the impact sensitivities of solid expls (see Vol 7, I42-R), PETN ranks as the most sensitive secondary expl (primary expls, such as Lead Azides, Mercuric Fulminate, etc, are more sensitive).

Aside from the question of how hot spots are formed, there is general agreement about the subsequent stages of the initiation of PETN by impact. Bowden & Yoffe (Ref 13), and more recently Bobolev et al (Ref 70) have observed the following sequential stages in the impact (also friction and spark) initiation of PETN layers:

1) Over a short time interval, deflagration near the point of initiation proceeds at several tens of meters/sec

2) At about 5-15mm from the point of initiation, the propagation velocity increases to several hundred meters/sec

3) At the end of the second stage there is a sharp increase in propagation velocity to about 1000m/sec. Depending on expl conditions, this "low velocity detonation" (LVD) can propagate over considerable distances, or it can go over into a normal detonation whose propagation velocity is determined by the density and dimensions of the PETN layer. It is possible to observe local ignitions ahead of the LVD front (Ref 70).

Bobolev et al (Ref 70) have shown that the LVD in stage 3 is a compression wave phenomenon and not a combustion front. For PETN they found that this compression wave must have a min velocity of 700-800m/sec, otherwise stage 3 cannot occur. They postulate that the initial combustion (stage 1) releases gaseous decomp products which raise the pressure of the reacting region and accelerate combustion. Hot combustion products penetrate into unreacted regions to produce new ignition sites and a further pressure increase, accelerated combustion, etc. This "avalanching" process accounts for stage 2. In an enclosed volume, i.e., in a cased charge, an accelerating flame front acts like a piston and drives a compression wave into the virgin material ahead of it. On attaining sufficient intensity this compression wave deforms and fragments the virgin material. Bobolev et al (Ref 70) claim that this deformation and fragmentation create new reaction sites (hot spots) in a manner similar to that postulated in Ref 85a. A balance between energy losses and energy release by the new reaction sites maintains the process at an approximately stable propagation velocity, namely the LVD of stage 3. If such a compression wave, travelling at around 1000m/sec in a confined layer of PETN at around 90% of crystal density, enters a region of lower density (80% crystal density or lower), Bobolev & Dubovik (Ref 48a) observed sharply accelerating propagation and establishment of normal detonation.

Some valuable insight into the mechanism of the initial hot spot formation (the processes preceding stage 1) during impact of PETN is provided by Heavens & Field (Ref 87). Their high-speed framing sequence of 5kg-1 meter impact on 15mgs of polycrystalline PETN shows: a) compression to a layer about 0.1mm thick; b) cessation of lateral spreading of the layer (about 10microsec after a) and jetting at 150m/sec; c) in an additional 10-15microsec the initially opaque PETN layer becomes gradually translucent, and completely transparent in 15-20microsec; d) transparency and rapid mobility of the PETN is associated with surface fusion followed by melting of the entire sample; and e) some 25microsec after b), the jetting velocity increases to 300m/sec, and some 5micro-
sec thereafter several initiation sites appear simultaneously, and burning at 300-400m/sec develops shortly thereafter.

Heavens & Field suggest that both gas cavities, sealed off during fusion of the sample, and high flow rate shearing near the impacting striker edge contribute to hot spot formation during PETN impact initiation.

Initiation by LASERS. Several investigators have used lasers (see Vol 7, L4) to initiate PETN. Brish et al (Ref 50) initiated detonation in PETN with Q-switched neodymium glass lasers (10600Å), focused to produce a power density in excess of 0.08MW/mm² at the surface of 5mm thick, 1 g/cc PETN samples. It appears that the delay in producing steady detonation under these conditions is of the order of 1.5 to 2 microsec. In a later study (Ref 69), using both neodymium glass and ruby lasers (6943Å), Brish et al found a critical diameter, d₀, for the laser initiation of PETN. For PETN with a specific surface of 550cm²/g (finer than normal production grade), d₀ ≥ 0.6mm. For finer PETN (larger specific surface), d₀ decreases. The laser energy required for initiation increases as the PETN packing density is increased. Brish et al claim that laser initiation is a thermal process, and that the laser energy rapidly absorbed in a thin layer of exp1 produces a shock wave which initiates detonation.

A series of papers by Menichelli & Yang (Refs 82, 84 & 86) showed that Q-switched ruby lasers could initiate steady detonation in PETN (and RDX or Tetryl) in <0.5 usec when a 1000Å thick Al layer was deposited on the face of the sample, and subsequently exposed to laser radiation of 0.5 to 4.2 J with a pulse width of 25 nanosec.

Initiation by Light. Neither Deb (quoted in Ref 19, p 111) nor the writer (Ref 47) could produce detonation of PETN exposed to high-intensity light. The writer used PETN cores at 0.8 to 1.5g/cc, with and without small additions of graphite (in attempts to increase light absorbency), in 1/4 inch ID plastic holders, and exposed them up to around 25 microsec to the radiation of Argon flash bombs (T=29000°C). In a few instances there was evidence of a deflagration, but no detonations were observed.

Initiation by Shock is undoubtedly the most quantitatively reproducible of all the modes of initiation. In spite of this there is still no general agreement as to its mechanism, although most authorities now agree that it is a thermal process. A distinction is usually made between homogenous and heterogeneous shock initiation. The former refers to initiation of single-phase liquids or single crystals, while the latter refers to initiation of cast, pressed or loosely-packed solid explos.

Generally, shock initiation measurements are carried out in a system consisting of a donor charge (some standard expl), an inert barrier, and an acceptor charge (test sample). The donor can be a plane wave expl lens (Ref 28) or an ordinary cylindrical charge (Ref 74, pp 220 & 261). The acceptor can be in the form of a wedge (Ref 28 & Ref 74, p 221) or a cylinder similar to the donor (Ref 74, pp 229 & 261). The cylindrical donor/barrier/acceptor systems are commonly called gap tests. Inert barriers are usually PMMA (polymethylmethacrylate) or brass. The information obtainable from plane wave shots and instrumented gap tests is: the input shock amplitude, and the run-up distance and time to detonation, if the shock is sufficiently strong to initiate detonation. In plane-wave/wedge shots one also obtains a record of the shock velocity during run-up. Obviously both types of tests, if made in sufficient numbers, provide a shock-initiation threshold. Shock initiation data are very reproducible in any given system, but can vary from system to system depending on test geometry, since test geometry controls rarefaction effects which in turn affect test results.

For single crystal PETN (a homogenous system) Campbell et al (Ref 28) indicate that a shock of 112kbar will produce detonation after a delay of about 0.3microsec. They claim that the initiation process is essentially identical to that observed by them in single-phase liquid expls. (see Vol 7, L31). Quantitative verification of their postulates is still in some doubt, because there is no general agreement about the temps that a 112kbar shock produces in the crystal, nor is there agreement about the values of the kinetic parameters that are necessary to compute the PETN thermal exl delay. However, in a qualitative sense their mechanism appears to be quite sound.

In their original publications (Ref 28) Campbell et al claimed that the shock initiation process
in heterogeneous expls is quite different from that of homogenous expls. Recent studies (Ref 74, pp 219, 321 & 435 and Ref 94), however, strongly suggest that shock initiation in expls pressed to 90% (or higher) of their crystal density is rather similar to that in homogenous expls, namely, that substantial reaction takes place well behind the shock front, and that stable detonation results when the compression waves produced by this reaction catch up with the initial shock front.

Exptl evidence showing that shock initiation in high density PETN pressings proceeds rather similarly to that in homogenous expls was obtained by the writer (Ref 74, p 219) and by Wackerle and coworkers (Refs 79 & 94). Fig 10, taken from Ref 74, summarizes the results of an instrumented gap test on unconfined one-half inch diameter 1.59g/cc PETN pressings. Quartz pressure gauges were placed on one face of the cylindrical PETN pressings of thickness h, while the other face was in contact with a PMMA barrier. All pressures are in the PETN either at the barrier/PETN interface (at h = 0), or at the PETN/quartz gauge interface (h > 0). The shock initiation threshold, $P_{50\%}$, is indicated by the horizontal striped band. In the bottom curve, with the input shock $P_0 > P_{50\%}$, the pressure decreases monotonically with h. In the next curve $P_0 = P_{50\%}$. Up to $h \leq 5$mm this curve parallels the bottom curve, but for $h \geq 5$mm the pressure rises rapidly. The dashed extrapolated portion is drawn to approach $x_t$, the run-up distance to detonation (also called build-up distance), asymptotically. The curve at $P_0 = 12$kbar may or may not have the "dip" as drawn. It certainly has a "dip" or a "flat" for $h \leq 2$mm. The top curve at $P_0 = 15$kbar (well above $P_{50\%}$) shows no indication of a "dip" or "flat". To ensure that the gauges produced no anomalous records at $P > P_{50\%}$, P-h curves were obtained with PMMA or (NH$_4$)$_2$SO$_4$ pressings substituted for the PETN. The PMMA Hugoniot in this low pressure region is fairly similar to that for 1.6 g/cc PETN (it lies slightly above the PETN Hugoniot in the P-u plane), and (NH$_4$)$_2$SO$_4$ has the same crystal density as PETN, and consequently qualifies as an inert "substitute" for PETN. Although not shown in Fig 10, the PMMA P-h curve for $P_0 < P_{50\%}$ is quite similar to the bottom curve of Fig 10. The main conclusion to be drawn from the data in Fig 10 is that at $P_0 = P_{50\%}$, for which half the samples tested detonate, the pressure in the PETN decreases during some 80 to 90% of the run-up distance before the pressure begins its rapid increase. This is certainly inconsistent with a shock front reaction, and strongly suggests that some type of disturbance occurring well behind the shock front sends out a pressure pulse that eventually overtakes the initial shock front.

Wackerle & coworkers (Ref 79) have photographically recorded a "second wave phenomenon" for 1.72g/cc PETN pressings, but not for 1.6g/cc pressings. However, in a later study (Ref 94) using quartz gauges to impact the PETN sample and shock it, as well as target gauges on the other PETN face, they found...
that 1.72g/cc and 1.6g/cc pressings behave quite similarly. Their data indicate a reaction-generated pressure pulse originating well behind the shock which eventually overtakes the initial shock front and initiates detonation.

It was already stated that shock initiation data are very reproducible within a system, but not necessarily reproducible among different systems. PETN appears to be somewhat of an exception — presumably because it is so "sensitive" (for lack of a better word). Generally, one expects a lower shock initiation "threshold" (see footnote (a) of Table 9) for plane wave systems than for small-scale unconfined gap tests. As shown in Table 9, the difference between the plane wave and unconfined gap test results for PETN is fairly small. As expected agreement between plane wave and confined gap test data is even closer. Examination of the last two rows of Table 9, and comparing them with the first three rows, suggests that preheating sensitizes PETN to shock more than by just decreasing its density (see below for a discussion of the density effect, although the data in Table 8 already suggest that PETN shock sensitivity increases as its packing density decreases). Shock sensitization by preheating was also observed for other explosives (Ref 74, p 219).

The shock sensitivity of PETN increases (i.e., the 50% firing stimulus decreases) as packing density decreases. This trait common to practically all exps, is illustrated in Fig 11.

The shock sensitivity of PETN increases slightly as PETN particle size is increased, i.e., as specific surface is decreased (Refs 34 & 74, p 265).

Chick (Ref 45, p 353) found that increasing the inert gas pressure in the interstices of a PETN pressing decreased its shock sensitivity. These effects were further examined by Dinegar et al (Ref 96), whose results are summarized in Fig 12. The desensitizing action of inert gases, and the sensitizing action of oxygen or air, in PETN pressings of about 3000cm²/g specific surface is quite similar to that shown in Fig 12 for about 12000cm²/g PETN, except that all curves are slightly displaced towards greater attenuator thickness (greater sensitivity) in accord with the results of Refs 34 & 74, p 265.

### Table 9

<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Packing Density (g/cc)</th>
<th>Specific Surface (cm²/g)</th>
<th>Shock Pressure Threshold (kbar)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane-wave</td>
<td>1.6</td>
<td>~3000</td>
<td>≥ 7 (a)</td>
<td>79 &amp; 94</td>
</tr>
<tr>
<td>Unconfined gap test</td>
<td>1.59</td>
<td>3350</td>
<td>9.1</td>
<td>74, p 227</td>
</tr>
<tr>
<td>Confined gap test</td>
<td>1.6</td>
<td>~</td>
<td>7.5 (b)</td>
<td>100a</td>
</tr>
<tr>
<td>Plane-wave</td>
<td>1.72</td>
<td>~3000</td>
<td>≥ 14</td>
<td>79 &amp; 94</td>
</tr>
<tr>
<td>Confined gap test</td>
<td>1.72</td>
<td>~</td>
<td>12 (b)</td>
<td>100a</td>
</tr>
<tr>
<td>Unconfined gap test</td>
<td>1.55</td>
<td>3350</td>
<td>6.7 (c)</td>
<td>74, p 224</td>
</tr>
<tr>
<td>Confined gap test</td>
<td>1.55</td>
<td>~</td>
<td>6.5 (b)</td>
<td>100a</td>
</tr>
</tbody>
</table>

(a) There is no real shock pressure initiation threshold in a plane-wave system. These are pressures in the region where the pressure-run up distance curve begins to be steep.

(b) Ref 100a does not specify whether these pressures are in the PETN or in the PMMA barrier. If these are PMMA pressures, the threshold pressures in the PETN would be lower than shown in the Table. The pressures in Refs 74 & 79 are pressures in the PETN at the PETN—barrier interface.

(c) PETN (originally at 1.59g/cc) pre-heated to 110°
Table 10
Relation Between Buildup Parameters for 1.6 and 1.72g/cm³ PETN

(Ref 94)

The coefficients listed were determined by non-linear least-squares fitting of the data of Ref 79, and have dimensions appropriate for $x_1$ in mm, $t_1$ in μsec, and $P_1$ in kbar.

<table>
<thead>
<tr>
<th>Density (g/cc)</th>
<th>Formulation</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>$x_1 = AT^B$</td>
<td>2.585</td>
<td>0.890</td>
</tr>
<tr>
<td></td>
<td>$x_1 = AP_1^{-B}$</td>
<td>567.1</td>
<td>1.985</td>
</tr>
<tr>
<td></td>
<td>$x_1 = AP_1^{-B}$</td>
<td>390.3</td>
<td>2.196</td>
</tr>
<tr>
<td>1.72</td>
<td>$x_1 = AT^B$</td>
<td>3.209</td>
<td>0.850</td>
</tr>
<tr>
<td></td>
<td>$x_1 = AP_1^{-B}$</td>
<td>593.2</td>
<td>1.678</td>
</tr>
<tr>
<td></td>
<td>$t_1 = AP_1^{-B}$</td>
<td>487.2</td>
<td>1.989</td>
</tr>
</tbody>
</table>

Algebraic expressions for run-up distances, $x_1$, and times to detonation, $t_1$, for the shock initiation of high density PETN pressings, taken from Wackerle & Johnson (Ref 94), are shown in Table 10. Although these parameters are for a plane-wave system, they agree quite well with the writer's gap test data (Ref 74) down to input pressures just slightly greater than $P_{50%}$.

Dinegar et al (Ref 34) found that at $P_0 > P_{50%}$, $t_1$ decreases as PETN specific surface is increased. For $P_0 >> P_{50%}$, $t_1$ is independent of specific surface.

Even if all the input shock energy of the data of Table 9 or Fig 11 went into the uniform heating of shocked PETN pressings, the resulting temp rises would amount to only several tens of degrees. This is, of course, grossly insufficient to produce any appreciable decomp in the PETN, to say nothing of decomp that is complete on a microsecond time scale, which is a typical $t_1$ for the shock initiation of PETN. The input shock must obviously produce localized and not bulk heating of the shocked material. How this occurs is still unclear. For example, Wackerle & coworkers (Ref 79) show that even
at $P_0 = 30$ kbar, the mean "bulk" temp rise for 1.6g/cc PETN is less than 200°C. For a single crystal at $P_0 = 112$ kbar they compute a $\Delta T = 420^\circ C$. This agrees roughly with a rather different method of computation made by Voskoboinikov et al (Refs 65 & 66) who get $\Delta T = 400^\circ C$ for $P_0 = 122$ kbar. However, Dremin et al (Ref 75), using yet another computational procedure, get $\Delta T = 170^\circ K$ at $P_0 = 100$ kbar and $\Delta T = 300^\circ K$ at $P_0 = 150$ kbar for single crystal PETN; and $\Delta T = 130^\circ K$ at 25 kbar, and $\Delta T = 230^\circ K$ at 50 kbar for PETN at 1.475g/cc. Obviously much work remains to be done before the mechanism of shock initiation of heterogeneous expls is fully understood.

VIII. Thermal Decomposition
A complete understanding of the initiation processes in an expl requires knowledge of its thermal decompn kinetics. Kinetic data are also necessary for the complete description of most facets of detonation phenomena, eg, detonation failure, diameter effect, LVD, etc. The thermal decompn kinetics of PETN have been studied repeatedly (Refs 10a; 10b; 20, pp 174-82; 26a; 38; 52; 62 & 106), but as yet there is no general agreement about the decompn mechanism or on the values of its Arrhenius parameters (see Vol 7, K9). Most of the above studies used manometric techniques to follow pressure changes during decompn. Cook (Ref 20) followed the reaction by measuring weight loss as a function of heating time. Rogers (Ref 106) employed DSC techniques (differential scanning calorimetry) to follow heat evolution as a function of time. The writer (Ref 10b) followed the
Fig 13  Thermal Decomposition of PETN
Fig 14  Arrhenius Plot for the Thermal Decomposition of PETN
decompn by chemical analysis of the PETN remaining after varying periods of heating. As will be shown below, the decompn is complex, involving retardation, autocatalysis, product interaction and other complications. Thus, it is more than pride of authorship that makes the writer suspicious of at least some of the conclusions of the indirect methods of following the decompn, and makes him favor the conclusion of his own direct method of chemically analyzing for the PETN remaining.

Most of the results of the writer's study are summarized in Figs 13 & 14. A closed system (an Al bomb of about 2.4 cc) was used in conjunction with a Wood's metal heat bath. After a given period of heating, the Al bomb was quickly placed in ice-water, opened, and the condensed residue removed. The PETN remaining was separated and analyzed by the FeCl₃-TiCl₂ method. In the studied temp range, decompn was for PETN in the liq phase (mp 141°), since even at the highest temp the PETN vapor press was only about 11 mm Hg (according to Ref 73).

The following conclusions may be drawn for the decompn without additives:

1) Above 185° the decompn is first order over its entire course.
2) At 181° and below the decompn is first order over 20 to 40% of its course, then it slows down and eventually re-accelerates above about 50% decompn.
3) The first order rate constant of
   \[ k_1 = 1.9 \times 10^{-13} \exp(-31600/RT) \]
   holds for all the data except at the highest (201°) and lowest (140°) temps. At 201° the observed rate constant is lower than expected (ie, decompn is slower than expected), probably because heat-up time of the sample is no longer negligible in comparison with the total heating time. At 140° there are insufficient data.
4) The effect of added surface (fine salt or powdered glass) is complex (not shown in Fig 13). At 171° the decompn with added surface at first (up to about 30% decompn) follows the 171° curve of Fig 13, then dips below it and finally (at about 50% decompn) rises above it.

Additives introduced into the bomb before heating provide some interesting data. Inert additives, such as cyclohexane or CO₂ (not shown in Fig 13), that raise the pressure in the bomb appear to make the decompn at 171° first order over its entire course (upper dashed line in Fig 13). In the presence of salt (NaCl), NO₂ addition [both (1.3 & 2.6) x 10⁻⁴ moles] acts the same way. In the absence of salt, however, 2.6 x 10⁻⁴ moles of NO₂ first slow down the 171° decompn, and then make it faster than first order. With 1.3 x 10⁻⁴ moles of added NO₂, the decompn (lower dashed line in Fig 13) is pseudo first order with an apparent induction time, or more probably a much slower decompn in its initial stages.

Not shown in Fig 13 is the effect of added water, which was found to greatly accelerate decompn at both 140° and 171°. Addition of 5 x 10⁻⁴ moles of acetaldehyde did not alter the initial decompn rate at 163°. However, addition of larger amounts (1.5 x 10⁻³ moles) produced expls. In a separate series of exprs, it was found that about 0.5 mole of NO₂ was formed for every mole of PETN decompd, and this ratio decreased rapidly in the middle stages of decompn and then increased again in the final stages.

The following macroscopic reaction scheme accounts for many of the observed effects (for simplicity PETN will be designated by RCH₂ONO₂):

(1) \[ RCH₂ONO₂ \rightarrow RCH₂\dot{O} + NO₂ \]
(2) \[ NO₂ + RCH₂\dot{O} \rightarrow RCH₂ONO₂ \]
(3) \[ RCH₂\dot{O} \rightarrow \text{intermediate decompn products (IDP)} \]
   such as H₂CO
(4) \[ IDP + NO₂ \rightarrow NO + N₂O + N₂ + CO + CO₂ + H₂O \]
(5) \[ RCH₂ONO₂ + H₂O \rightarrow RCH₂OH + HONO₂ \]
(6) \[ H₂O + 3NO₂ \rightarrow 2HNO₃ + NO \]

There is general agreement about step (1). Step (2) is supported by the observed slowing down of the initial decompn stages when NO₂ is added. It is also supported by Levy's studies of the decompn of ethyl nitrate (Ref 15b). At the higher temps, steps (3) and (4) remove both RCH₂\dot{O} and NO₂ so rapidly that there is essentially no back reaction (step 2). Thus the reaction is first order (step 1) over its entire course. It would appear steps (3) and (4) are heterogeneous reactions (at least at lower temps) that are favored by the combination of added surface and increased pressure (upper dashed line in Fig 13). The reacceleration
of the decompn in its final stages at temps of 181° and below (the reacceleration is off-scale for the 149° and 163° curves in Fig 13) could be due to hydrolysis (step 5) after enough water had been produced via (4) and nitric acid via (6), since hydrolysis is much faster in acidified water. This supposition is supported by Andreiev & coworkers (Refs 26a & 38) who showed that the hydrolysis reaction accelerates PETN decompn at the lower decompn temps.

In the writer's study, the addition of NO₃ most likely also introduced small amounts of water and/or nitric acid. These impurities could possibly account for the accelerated decompn rate observed in the middle and later stages of expts with added NO₃, but without salt. It is not clear why the presence of salt apparently prevents the hydrolysis reaction (see Fig 13 – with salt & NO₃ the decompn is first order over its entire course).

At the highest temps, water will be mostly in the vapor state (eg, at 185° the vapor pressure of water is about 11 atm while the estimated pressure in the bomb of the gaseous products for 50% decompn is about 6 atm) while the PETN is still liq. Thus the hydrolysis reaction does not take place unless there is appreciable soln of water vapor in the liq PETN. At 163° the vapor pressure of water is roughly equivalent to the total pressure in the bomb at 50% decompn. Thus, for the hydrolysis reaction to be significant at lower temps, but not at higher temps, there must be appreciable solubility of water vapor in liq PETN in the 160–70° temp range, and at lower temps, but not at temps above 185°.

In Ref 10b the step
\[ RCH₂ONO₂ + RCH₂OH = RCH₂OH + RCHONO₂ \]
was proposed as part of the decompn scheme. We now rule it out in view of the convincing evidence by Levy (Ref 15b) that the analogous step is absent in the ethyl nitrate decompn. However, some RCH₂OH may form via step 5. It, or further hydrolysis products should be water soluble. Water soluble nitrate-containing material was found in the wash water during separation of PETN from the rest of the residue in the bomb.

By analogy with Levy's studies we might expect the formation and subsequent decompn of nitrite esters:

\[ RCH₂O + NO = RCH₂ONO \]

It has been suggested (Ref 38) that the above reaction may proceed differently:

\[ RCH₂O + NO = RCHO + NOH \]

\[ 2NOH = N₂O + H₂O \]

This sequence could account for some of the reacceleration in the late decompn stages (when there is appreciable NO via step 4) by removing RCH₂O, thus preventing step 2, and by providing H₂O for hydrolysis. The sequence could also account for N₂O, which is a known decompn product.

According to Andreiev and coworkers (Refs 26a & 38) and Kaidymov (Ref 62) the decompn of solid PETN is much slower than that of molten PETN. They suggest that partial melting occurs during decompn at temps below the PETN mp and this increases the decompn rate. The increase in the PETN decompn rate in the presence of TNT (observed by Urbanski et al, Ref 3) is claimed to be brought about similarly, i.e., the PETN–TNT system forms low melting eutectics and PETN decompn proceeds, in effect, in a TNT soln (Ref 38).

The published PETN Arrhenius parameters are quite horrendous. They are summarized in the tabulation below:

<table>
<thead>
<tr>
<th>Refs</th>
<th>Technique</th>
<th>E (kcal/mole)</th>
<th>Z (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Robertson (10a)</td>
<td>Manometric</td>
<td>47,000</td>
<td>10¹⁹.8</td>
</tr>
<tr>
<td>Robertson (10a)</td>
<td>Manometric</td>
<td>39,500 (a)</td>
<td>10¹⁶.1</td>
</tr>
<tr>
<td>Rogers (106)</td>
<td>DSC</td>
<td>47,000</td>
<td>10¹⁹.8</td>
</tr>
<tr>
<td>Cook (20)</td>
<td>Weight Loss</td>
<td>38,600</td>
<td>10¹⁵.2</td>
</tr>
<tr>
<td>Andreiev (26a)</td>
<td>Manometric</td>
<td>39,000</td>
<td>10¹⁵.6</td>
</tr>
<tr>
<td>Andreiev (26a)</td>
<td>Manometric</td>
<td>40,100 (b)</td>
<td>10¹⁵.8</td>
</tr>
<tr>
<td>Roth (10b)</td>
<td>Chemical Analysis</td>
<td>31,600</td>
<td>10¹³.3</td>
</tr>
</tbody>
</table>

(a) 5% solution in dicyclohexylphthalate
(b) 5% solution in TNT

It is instructive to compare, insofar as possible, the gaseous products of PETN decompn and expln. This is done on a water-free basis in Table 11. Note the absence of oxides of nitrogen in the expln products and the increase in CO₂ from decompn to expln.
Table 11
Gas Compositions of PETN Decomposition and Explosion
(Water-free Basis; in Mole %)

<table>
<thead>
<tr>
<th></th>
<th>NO₂</th>
<th>NO</th>
<th>N₂O</th>
<th>N₂</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Decomposition</td>
<td>12.0</td>
<td>47.6</td>
<td>9.5</td>
<td>1.6</td>
<td>6.3</td>
<td>21.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Impact (Ref 13, p 96)</td>
<td>24.3</td>
<td>5.3</td>
<td>9.4</td>
<td>19.1</td>
<td>35.4</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Explosion in Calorimeter (unconfined sample) (Ref 52a)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>26.3</td>
<td>46.1</td>
<td>20.9</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Effect of Irradiation with Nuclear Particles

Decomp of expls can be induced by irradiation with nuclear or atomic particles (Ref 19, pp 113–21). Urizar et al (Ref 31a) found that neutron irradiation produces about 14% weight loss in PETN, mostly as CO₂. Some Petrin and PE-dinitrate were formed.

The effect of nuclear reactor irradiation on PETN was studied by Avrami and Voreck (Ref 71a). Weight losses ranged from 3.65% for an 8.7 minute irradiation (0.61 x 10⁸ R gamma) to 10.53% for 25 minutes (1.78 x 10⁸ R gamma). Infrared, DTA and mp data revealed that the decomp of PETN increased greatly as a function of total dose. For example, at the 25 minute exposure (1.9 x 10⁻¹⁶ nvt, fast neutrons and 1.76 x 10⁸ R gamma), the mp was decreased by 7–13⁰.

Avrami et al (Ref 96a) made an extensive study of the effects of ⁶⁰Co irradiation on both powdered and pelletized expls. For PETN they found significant changes even at their lowest radiation exposure of 1 x 10⁷ R [1 R (of dry air) = 87.7 ergs (absorbed)/g]. At 9 x 10⁷ R there was 7.1% weight loss and swelling of the pellets. Irradiation up to 9 x 10⁷ R produced little change in the PETN DTA thermogram. In TGA (thermogravimetric analysis) measurements, irradiation drastically reduced the onset of decomp — from 160 to 173⁰ for unirradiated samples, to 70⁰ for samples irradiated at 9 x 10⁷ R. Total weight loss or temp for 10% weight loss were, however, not greatly affected by irradiation. Irradiation at 9 x 10⁷ R lowered the mp by 5⁰, and irradiation at 1.06 x 10⁸ R reduced the PETN to a white sticky paste. There is some indication that irradiation increases PETN impact sensiti-}

vity, although the real effect was to make the already erratic impact results even more erratic. Irradiation at 9 x 10⁷ R lowered the 5 sec expln temp from 228 to 222⁰ — an almost insignificant effect. However, the slope of the log expln time vs 1/T plot appeared to be less for the irradiated samples (large scatter in the measurements) than for the controls. The detonation velocity of PETN pellets irradiated at 9 x 10⁷ R was about 400m/sec lower than the controls

Explosion Temperature is not a precisely defined entity, since it depends on test geometry, heating rate, etc. It is better to speak of an explosion temp after a certain heating time, eg, 1 sec-expln temp, 5 sec-expln temp, etc. An even better procedure is to plot the log of expln time vs 1/T. These plots are generally linear.

For PETN we obtain the following 1 sec and 5 sec “expln temps” from various sources:

Table 12
PETN “Explosion Temperatures”

<table>
<thead>
<tr>
<th></th>
<th>1 sec Expln Temp °C</th>
<th>5 sec Expln Temp °C</th>
<th>Min Observed Expln Temp °C</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>255</td>
<td>222</td>
<td>215</td>
<td></td>
<td>13a</td>
</tr>
<tr>
<td>—</td>
<td>225</td>
<td>—</td>
<td>10b</td>
<td></td>
</tr>
<tr>
<td>—</td>
<td>225</td>
<td>205-215</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>276</td>
<td>228</td>
<td>&lt; 214</td>
<td>96a</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>227</td>
<td>175</td>
<td>32b</td>
<td></td>
</tr>
</tbody>
</table>

Lee et al (Ref 74, p334) find that expln temps of PETN increase as the ambient pressure on the sample is increased. Bowden and Yoffe (Ref 19, p40) also observed this effect.
IX. Combustion & DDT

Combustion.

PETN is difficult to ignite at atm pressure. According to Andreev (quoted in Ref 44, p 185), PETN will not burn even in a tube as large as 18mm diameter unless it is preheated to 95°; then burning propagates at the low rate of about 0.05cm/sec. Andreev & Popova (Ref 30b) found that the mass burning rate of 1.25 to 1.3g/cc PETN pellets follows the linear burning rate law,

$$u_m = 0.0193P$$

over the range of 16 to 750 atm (where the mass burning rate $u_m$ is in g/cm²/sec and the ambient pressure $P$ is in kg/cm²). At 1 atm and room temp the critical diameter for PETN was 30mm. Molten PETN burns more readily and its burning rate approaches that of NG and EGDN. Taylor (Ref 32) gives a mass burning rate of 0.86g/cm²/sec for 1.25g/cc PETN at 52 atm. This agrees fairly well with the 1.00g/cm²/sec computed by the Andreev-Popova rate law shown above. Actually, packing density appears to have little effect on mass burning rate, eg, Taylor finds $u_m = 0.99, 0.86$ & 0.99g/cm²/sec respectively for 0.67, 1.25 & 0.95g/cc pellets (of about 5 micron particle size PETN). He ascribes this apparent constancy of $u_m$ to the formation of a continuous layer of molten material over the burning expl. Heat transfer from the gas phase burning reactions to the solid, now controlled by this molten layer and essentially independent of the physical state of the solid, becomes nearly constant. A constant heat transfer implies a constant mass burning rate. However, if this molten layer becomes too thin (in comparison with pore diameter), convective burning can be established and burning rates will increase sharply (Ref 31). In convective burning, propagation is via the flow of hot gases thru the pores of the burning material at a speed determined by the existing pressure gradients. Similar conclusions were reached by Belyaev et al (Ref 37) in their study of PETN combustion in a manometric bomb. For PETN of about 0.1 micron pore size, transition to convective burning occurs at pressures of about 330 bars. Taylor (Ref 24, p 79 & Ref 31) gives the following mass burning rates for 500-853 micron PETN at around 0.92g/cc:

<table>
<thead>
<tr>
<th>Pressure (psig)</th>
<th>Burning rate (g/cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>0.53</td>
</tr>
<tr>
<td>525</td>
<td>13.9</td>
</tr>
<tr>
<td>750</td>
<td>59.0</td>
</tr>
</tbody>
</table>

Obviously the pressure dependence of the burning rate in Taylor’s expts with porous PETN is much greater than linear.

The development of combustion in PETN by shock was studied by Dubnov et al (Ref 93). Unfortunately, the original article is unavailable to us, but it appears that the effects of incident shock velocity, reflected shock pressure and temp, surrounding gas, and surface roughness of the PETN were examined.

Deflagration-to-Detonation Transition (DDT)

DDT is discussed in some detail in Section VII of the article on Propellants, Solid in this Vol. That discussion emphasized the importance of convective burning. A convective flame front is an ignition wave which is propagated by the passage of hot combustion gases thru the pores of the expl mass, with the hot gases being forced into the pores by confinement. However, this penetration does not result in the immediate formation of a flame front. The gases heat the pore walls and are consequently cooled. It is the continuous flow of gases which raises the pore wall temp sufficiently to produce ignition, and the avalanching of such a process produces what becomes the head of the convective front. At some later time compressive waves develop in the region behind the convective flame front. These waves coalesce and reinforce each other, and eventually produce a shock which overtakes the convective flame front, and shortly thereafter a shock-to-detonation transition occurs.

DDT in PETN has been the subject of many studies (Refs 10c, 13, 24b, 35, 36, 67, 68 & 70). The highlights of these investigations, most of which favor the DDT process outlined above, are presented below.

Griffith & Grocock (Ref 24b) found that the DDT run-up distance decreases as packing density is increased but at high packing density DDT is difficult to achieve. The particle size—run-up distance curve goes thru a minimum, with the optimum PETN size falling in the range of 76–124 microns. Streak camera records show detonation starting well ahead of the flame front.

Andreev & Chuiko (Ref 35) observed stable burning in PETN of 5 micron particle size and relative density δ = 1.17, up to 60 atm pressure. At higher pressures (up to 100 atm) burning rate increased rapidly. The pressure at which transition from stable to accelerating...
burning occurs increases with $\delta$ and decreases as particle size is increased.

Andreev & Gordunov (Ref 36) define a critical pressure $P_c$ above which the pressure in the burning PETN increases drastically in a short time interval $\tau$.

The studies of Bobolev et al (Ref 70) on the transition from burning to detonation have already been described in Section VIII under *Initiation by Impact & Friction*.

Korotkov et al (Ref 67) also stress the importance of convective burning in DDT. They claim that the length of the run-up zone to detonation is determined by $dp/dt$ in the burning zone. The value of $dp/dt$ in turn is determined by the specific burning surface and the permeability, pore size and compressibility of the expl.

In a subsequent study (Ref 68) these authors formulate the DDT model shown in Fig 15. In this model, Region I is surface combustion; Region II, convective combustion with a ragged front; Region III, convective combustion with a smooth front; Region IV, LVD; and Region V, detonation. Surface combustion is propagated by heat conduction, while propagation in Region (Ref 70), Obmenin et al (Ref 68) find that the critical velocity for establishing LVD (Region IV) in PETN, of 500 micron particle size and porosities of 0.04 to 0.2, is 800 m/sec. High porosity, large charge diameter and long columns favor DDT. For PETN, the min porosity for DDT is 0.18 for 10mm diameter charges. LVD depends on confinement material. Thus LVD is 900, 2600 & 3200 m/sec respectively for low-porosity PETN in Plexiglas, brass and steel. LVD in PETN is not affected by decrease in particle size or increase in charge diameter. However, in metal confinement, DDT occurs at lower porosities than in Plexiglas, probably because higher pressure can be achieved before the confining tube ruptures. The max pressure in the confining tube prior to rupture also appears to control the actual velocity of the LVD regime (as shown above, the LVD in steel is higher than the LVD in Plexiglas).

Related to both DDT and initiation by shock is the initiation of solid expls by gas detonations. Weiss et al (Ref 61) found that PETN at 0.7 g/cc could be initiated by a gas detonation of 21 atm initial pressure, which produced an initial (presumably in the PETN) pressure of 2 kbar. Under these conditions initiation delay in the PETN was less than one microsecond.

Written by J. ROTH

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**X. Refs:**

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16, 359 (1936); 25, 257 (1957) & CA 28, 27 (1934)
5) L. Desvergnes, ChimInd(Paris) 29, 1263 (1933) & CA 27, 4675 (1933)
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7) T. Urbasiński et al, SS 32, 1 (1937) & CA 31, 4497 (1937)
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10A) A.J.B. Robertson, JSocChemInd(London) 61, 221 (1948) & CA 43, 405 (1949)
10B) J. Roth, Addendum to
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3) A. Stettbacher, “Pentaerythritoltetranitrate As a Military Explosive”, ZAngChem 41, 716-9 (1928) & CA 22, 3991 (1928)
5) F.M. Jaeger, “Tetrahedral of Pyramidal Structure of Methane Derivatives”, ChernWbl 27, 50-2 (1930) & CA 24, 2350 (1930)
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10) J. Meisner, GerP 539175 (1929) & CA 26, P1621 (1932)
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12) G. Guastalla & G. Raccin, “Modern Explosives”, IndChem (Italian) 8, 843-8 (1933) & CA 27, 5189 (1933)
13) Ibid, “Modern Explosives II”, IndChem (Italian) 8, 973-82 (1933) & CA 27, 5189 (1933)
15) J.F. Roth, “A Laboratory Method For Determining Velocity of Detonation Using Short Columns (of Explosives)”, SS 28, 42-6 (1933) & CA 27, 2579 (1933)
16) T.R. Patterson, BritP 378500 (1932) & CA 27, P3950 (1933)
18) T.R. Patterson, USP 1933754 (1934) & CA 28, P646 (1934)
19) P.R. DeWilde, “Continuous Commercial Manufacture of Nitropentaerythritol And The Future of This Explosive”, Chim&Ind (Paris) 30, 1034-7 (1933) & CA 28, 1863 (1934)
27) M. Tonegutti, “Heat of Explosion of Tetrinitropentaerythritol And Trimethylenehexanitramine”, SS 32, 93-7 (1937) & CA 31, 6465 (1937)
28) A.P. Challenor, BritP 461641 (1937) & CA 31, 5385 (1937)
30) T. Urbanowski & W. Malendowicz, “Influence of Ultraviolet Rays on a Few Explosives”, RoczChem 18, 856-63 (In Fr, 864-3)


Pentaerythritol Tetra-acetate (PETA). C15H20O6, mw 304.29, OB to CO2 =147.4%; needles, mp 83-4°; (Refs 1 & 2); prep'd by the action of Ac2O on PE in the presence of Na acetate (Ref 2). The IR absorption peaks are given in Ref 5; CA Registry No 597-71-7

To evaluate its use as a plasticizer for NC, a mixt of 70% NC and 30% PETA was examined by the vac stability test at 110°. The gas evolution vs time curve was found to be slightly concave downward with a value of 7.5ml of gas/g after 80 hours (Ref 4). Comps of 50-64% NC, 28-42% NG, and 2-8% PETA have been patented as rocket propilnts (Ref 3); and comps of 50-80% TNT or PETN and 20-50% PETA as bursting explos (Ref 3). Other comps of 15-60% TNT or PETN, 20-80% AN, and 5-25% PETA are in the same patent


Pentaerythritol Acetate Trinitrate. C15H22N3O11, mw 313.18, N 13.4%; OB to CO2 =43.5%; a cryst solid, mp 87-8°. It has been prep'd by the nitration of PE monoacetate with 100% nitric ac at 0°, yield 99% (Ref 3); by the nitrolysis of PE monoacetate cyclic arsenite, yield 97% (Ref 5); or by the acetylation of Petrin with Ac chloride (Ref 2), or Ac2O (Ref 4). In the latter ref the acetate is used as a deriv for the iden of Petrin. Its Qe is 845cal/g. It has a Taliani slope of 0.27mm/min at 110°, and has a 17min K1 test at 82° (Ref 2)

Pentaerythritol Allyl Ether Trinitrate. \( C_8H_{13}N_3O_{10} \), \( m w 311.21, N 13.5\% \), OB to \( CO_2 \) -64.3\%; a liq, d 1.373g/cc at 20°, RI 1.4797 at 20° (Ref 3), visc 66 centipoises at 20° (Ref 2); prep'd by the nitration of PE monoallyl ether (Ref 3)

Explosive Properties:

Brisance by Sand Crushing Test. A 0.5g sample when initiated with 0.5g of MF crushed 7.4g of sand (NG 53.5g) (Ref 2)

Drop Test by Filter Paper Method. 175mm for 100% explns (NG 100mm) (Ref 2)

Friction Sensitivity by Sliding Rod Test. At a 75° angle and a 10 lb wt, no explns in 5 tries (NG 5 explns in 5 tries) (Ref 2)

Heat of Combustion. 3437cal/g (Ref 2)

Heat of Explosion. 837cal/g (Ref 2)

Methyl Violet Heat Test at 120°. 285 min (propyl ether trinitrate 120 min (NG 65 min).

It is suggested that the unsaturated allyl group has a stabilizing effect giving an improved heat test (Ref 2)

Uses. It has been proposed as a high energy plasticizer for NC for use in rocket proplnts (Ref 2)


Pentaerythritol Formate Trinitrate. \( C_6H_9N_3O_{11} \), \( m w 299.16, N 14.1\% \), OB to \( CO_2 \) -29.4%; a solid, mp 62-3°; prep’d by the action of 90% formic ac on Petrín in the presence of sulfuric acid, yield 84.1% (Refs 2 & 3)

Refs: 1) Beil 2, (38) 2) N.S. Marans et al, JACS 76, 1304 (1954) 3) Urański 2 (1965), 193

Pentaerythritol Methacrylate Trinitrate. \( C_9H_{13}N_3O_{11} \), \( m w 339.22, N 12.4\% \), OB to \( CO_2 \) -63.7%; a colorless to yellow liq, d 1.435g/cc at 20°, RI 1.4918 at 20°, CA Registry No 19363-43-3

Prep’d by the action of methacryl chloride on Petrín, yield 82.5% (Refs 2 & 3). It is readily polymerized to an insol flammable polymer (Ref 3) which has been patented as an ingredient in high energy rocket propiints (Ref 4)


Pentaerythritol Methyl Ether Trinitrate. \( C_9H_{12}N_3O_{10} \), \( m w 285.17, N 14.7\% \), OB to \( CO_2 \) -42.1%; a solid, mp 79-80° (Ref 3); prep’d by the nitration of PE monomethyl ether (Ref 4). Impact sensy using a 2kg wt 165cm for no explns (PA 35cm); power by Pb block expansion 128% of PA, 133% of TNT (Ref 3). It has been patented as an ingredient for expls, propilnts, and ign devices (Ref 2)


Pentaerythritol Monochlorohydryd Trinitrate [2-Chloromethyl-2-hydroxymethyl-1,3-propanediol Trinitrate (Name preferred by CA)]. \( C_5H_5ClN_3O_3 \), \( m w 289.59, N 14.5\% \), OB to \( CO_2 \) -24.9%; a white cryst solid, mp 65-6° (Ref 3); prep’d by the action of P pentachloride on Petrín, yield 22.5% (Ref 3). It has been patented as an ingredient for expls, propilnts, and ign devices (Ref 2). For the expl props of a mix of this compd with PE dichloride dinitrate, see above under the latter name


Pentaerythritol Nitrobenzoates Trinitrate. Ortho-Nitrobenzoate. \( C_{12}H_{12}N_4O_{13} \), \( m w 420.24, N 13.3\% \), OB to \( CO_2 \) -64.8%; a solid, mp 94-5°; prep’d by the action of o-nitrobenzoyl chloride on Petrín in pyridine, yield 64% (Ref 3)

Meta-Nitrobenzoate. A solid, mp 102-3°, prep’d the same way as the ortho isomer using m-nitrobenzoyl chloride, yield 71% (Ref 3). Impact sensy with a 2kg wt, no explns at 175cm
Para-Nitrobenzoate. A solid, mp 106–8°; prepd the same as above using p-nitrobenzoyl chloride, yield 60%. Urbanskis states that this compd has great expl strength and low sen to shock (Ref 4)

3,5-Dinitrobenzoate, C$_1$H$_{11}$N$_5$O$_{15}$, mw 465.24, N 15.1%, OB to CO$_2$ –49.9%; a solid, mp 109–10°, prepd the same as above using 3,5-dinitrobenzoyl chloride, yield 70% (Ref 3)

Refs: 1) Bell, not found 2) Blatt, OSRD 2014 (1944) (found on Class of Compounds page “Nitrates") 3) N.S. Marans et al, JACS 76, 1304 (1954) 4) Urbanski 2 (1965), 193

Pentaerythritol Tetrabenzate, C$_{33}$H$_{28}$O$_8$, mw 552.55, OB to CO$_2$ –208.5%; needles, mp 99–101°; prepd by the action of Bz chloride on PE (Refs 1 & 2). A mixt of PETN with PE tetrabenzoate and a PE pyromax (structure unspecified) has been patented as a progressive burning gun propnl (Ref 3)

Refs: 1) Bell 9, 144 & 688 2) P. Rave & B. Tollens, Ann 276, 61 (1893) 3) T.L. Davis, USP 1432321 (1923) & CA 17, 472 (1923)

Pentaerythritol Tetramis (4,4,4-trinitrobutyrate), C$_{2}$H$_{24}$N$_{12}$O$_{32}$, mw 972.40, N 17.3%, OB to CO$_2$ –36.2%; w crystals from glce ac, mp 0.5

O$_2$N
(0$_2$NCCCH$_2$CH$_2$COCH$_2$)$_4$C

O$_2$N

174–5° (Ref 2); prepd by the addn of nitroform to PE tetra-acrylate, yield 41.6% (Ref 2); Q$_{e}$ 904cal/g (Ref 3). The compd was incorporated at a level of 10% in a NG/NC propnl formulation. The burning rate vs temp curve was plotted and was found to increase from 0.26 inches/sec at 300psi to 0.79 inches/sec at 4000psi (Ref 3)


Pentaerythritol Diacetate Dipropionate (Penta-

Pentaerythritol Acetate Propionate, PEAP). C$_{1}$H$_{2}$O$_{9}$, mw 348.38, OB to CO$_2$ –174.7%; a liq, bp 173–80° at 2mm (Ref 2); prepd by the reaction of PE with two moles of Ac$_2$O, then two moles of propionic anhydride, or by the reaction of PE with an equimol mixt of the two anhydrides (Refs 3 & 4). The analysis of a coml sample of PEAP is given in Ref 5, and the Specs for PEAP for use in proplnt powd are in MIL-P-23313 (22 Jan 1962). It has been used instead of triacetin in casting liq (see under “Cast Propellants” in Vol 2, p C84) for the prep of proplnt grains for Terrier sustainer. For specific formulations see Refs 6 & 7 in the closed literature


Pentaerythritol Propionate Trinitrate.

C$_{8}$H$_{13}$N$_{3}$O$_{11}$, mw 327.21, N 12.8%, OB to CO$_2$ –56.3%; a solid, mp 39–40° (Ref 3); prepd by the action of propionyl chloride on Petr in eth, yield 83% (Ref 3); Q$_{e}$ 663cal/g; Taliani test 0.25ml of gas evolved/min at 110°; KI test 20 min at 82° (Ref 2)

Refs: 1) Bell, not found 2) Anon, ABL MPR No 6 (Apr 1952), 8 3) N.S. Marans et al, JACS 76, 1305 (1954)

Pentaerythritol Propyl Ether Trinitrate.

C$_{8}$H$_{13}$N$_{3}$O$_{10}$, mw 313.22, N 13.4%, OB to CO$_2$ –69.0%; a liq, d 1.332g/cc at 20°, RI 1.4654 at 20° (Ref 3); visc 66 centipoises (Ref 2); prepd by the nitration of PE propenyl ether (Ref 3) Exptl Properties:

Brisance by Sand Crushing Test. A 0.5g sample when initiated with 0.5g of MF crushed 6.1g of
sand (NG 53.5g) (Ref 2)

Drop Test Using Filter Paper Method. 200mm for 100% expls (NG 100mm) (Ref 2)

Friction Sensitivity by Sliding Rod Test. At a 75° angle & a 10 lb wt, no expls in 5 tries (NG 5 expls in 5 tries) (Ref 2)

Heat of Combustion. 3540cal/g (Ref 2)

Heat of Explosion. 804cal/g (Ref 2)

Methyl Violet Heat Test at 120°. 120 min for color change (NG 65 min) (Ref 2)

Uses: It has been proposed as a high energy plasticizer for NC to be used in rocket proplnts (Ref 2)


Pentaerythritol Trinitrate Tris(difluoramino) methyl Ether (FA-PETRIN). C₆H₈F₆N₆O₁₀, mw 438.16, N 19.2%, OB to CO₂ -11.0%; a

\[
\text{CH}_2\text{ONO}_2
\]

\[
\text{(F}_2\text{N)}_3\text{COCH}_2\text{CCH}_2\text{ONO}_2
\]

\[
\text{CH}_2\text{ONO}_2
\]

shock sens liq, prepd by the addn of perfluoroguanidine to Petrin, followed by fluorination of the adduct (for refs to the prep of this type cmpd see under Penterythritol Mononitrate, FA-PEMON)

Exp! Properties. Qₚ -136kcal/mole, Qₜ 1535 cal/g; impact sensy on PA app 5.6cm (NG 10cm), on Bruceton app 2.1cm (NG 10cm)


Pentaerythritol Tetrazis[tris(difluoramino) methyl Ether] (FA-PE). C₆H₈F₂₄N₁₂O₄ mw

\[
\text{F}_2\text{N}
\]

\[
\text{(F}_2\text{NCOCH}_2\text{C})_4\text{C}
\]

\[
\text{F}_2\text{N}
\]

804.19, N 20.9%, OB to CO₂ & HF -11.9%; a shock sens solid, mp 53-4°, vap press below

0.05mm at 25° (Ref 2); prepd by the addn of perfluoroguanidine to PE followed by fluorination of the adduct (Ref 2). For examples of the prepn of this type cmpd see Refs 3, 4 & 5

Exp! Properties. Qₚ -172kcal/mole, Qₜ 1659 cal/g, impact sensy on PA app below 1 cm (PETN 50cm, NG 10cm) (Ref 2)


Pentaerythritol Vinyl Ether Trinitrate [2-(Hydroxymethyl)-2-(vinlyoxymethyl)-1,3-propanediol Trinitrate (name preferred by CA)]

\[
\text{C}_7\text{H}_{11}\text{N}_3\text{O}_{11} , \text{mw 297.18, N 9.43%, OB to CO}_2
\]

\[
\text{CH}_3\text{ONO}_2
\]

\[
\text{CH}_2\text{:CHOCH}_2\text{CCH}_2\text{ONO}_2
\]

\[
\text{CH}_2\text{ONO}_2
\]

-51.2%; a solid, mp 54-5°; CA Registry No 22769-89-7

It is prepd by the interaction of vinyl 2-chloroethyl ether and Petrin in methyl alc catalyzed by a mixt of Hg and Na acetates. 

Qₚ 2982cal/g, Qₜ 855cal/g; impact sensy with 1 kg wt 20.8 inches for 50% expls; Taliani test: 

\[ m_{100} = 0.050, t_{100} = 5.5 \text{ hrs} \]

It can be polymerized and copolymerized with acrylates to give useful proplnt ingredients

Refs: 1) Beil, not found 2) S.F. Reed, USP 3427295 (1969) & CA 70, 96158 (1969)

Pentaerythritol Diglycolate Tetranitrate.

\[
\text{C}_9\text{H}_{12}\text{N}_4\text{O}_{16} , \text{mw 432.21, N 13.0%, OB to CO}_2
\]

\[
(\text{O}_2\text{NOCH}_2\text{COCH}_2\text{J}_2\text{CCH}_2\text{ONO}_2
\]

\[
\text{-29.6%; power by Pb block expansion is 79% of PA}
\]

Refs: 1) Beil, not found 2) Blatt, OSRD 2014 (1944) (found on Class of Compounds page "Nitrate")
Pentaerythritol Monolactate Tetranitrate.

\[ \text{C}_6\text{H}_{13}\text{Na}_4\text{O}_{14}, \text{ mw } 388.21, \text{ N } 14.4\%, \text{ OB to CO}_2 -33.0\%; \text{ a liq, prep by the nitration of PE} \]

\[ \text{CH}_2\text{ONO}_2 \]

\[ \text{O} \]

\[ \text{CH}_3\text{CHCOCH}_2\text{CH}_2\text{ONO}_2 \]

\[ \text{ONO}_2 \]

\[ \text{CH}_2\text{ONO}_2 \]

monolactate. A mixt of this compd with a small amt of PE dilactate tetranitrate has been patented as an expl plasticizer for NC and Nitrostarch

Refs: 1) Beil, not found 2) J.A. Wyler, USP 2086146 (1937) & CA 31, 6010 (1937)

Pentaerythritol Tetralactate Tetranitrate [Pentaerythritol Tetrakis (2-nitroxypropionate)].

\[ \text{C}_7\text{H}_{24}\text{Na}_4\text{O}_{20}, \text{ mw } 404.37, \text{ N } 13.9\%, \text{ OB to CO}_2 -103.0\%; \text{ prep by the nitration of PE} \]

\[ (\text{CH}_2\text{CHCOCH}_2)_4\text{C} \]

\[ \text{O} \]

\[ \text{NO}_2 \]

tetralactate with mixed ac. Other nitrated PE esters of hydroxy acids are also claimed. The compds are useful expl ingredients

Refs: 1) Beil, not found 2) J.A. Wyler, USP 2086146 (1935) & CA 31, 6010 (1937)

Pentaerythritol Monoglyceryl Ether Pentanitrate.

\[ \text{C}_8\text{H}_{15}\text{N}_5\text{O}_{16}, \text{ mw } 435.21, \text{ N } 16.1\%, \text{ OB to CO}_2 -23.9\%; \text{ a solid, mp } 54.5-5.0^\circ, d 1.57 \text{g/cc at} \]

\[ \text{CH}_2\text{ONO}_2 \]

\[ \text{O}_2\text{NOCH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{ONO}_2 \]

\[ \text{ONO}_2 \]

\[ \text{CH}_2\text{ONO}_2 \]

20°, RI 1.531 at 31° (Ref 3); prep by the hydroylation of PE monoglyl ether followed by nitration of the pentahydrate compd (Ref 3). Other phys and expl props are given in Ref 2

Refs: 1) Beil, 1(2816) 2) Anon, SPIA M3a (June 1949), Unit 119 (Conf) 3) R. Evans & J.A. Gallaghan, JACS 75, 1248 (1953)

Pentaerythritol Diglycerol Ether Hexanitrate.

\[ \text{C}_{11}\text{H}_{24}\text{Na}_4\text{O}_{20}, \text{ mw } 554.30, \text{ N } 15.16\%, \text{ OB to CO}_2 -31.7\%; \text{ a liq, d } 1.54 \text{g/cc at } 20^\circ, \text{ RI } 1.4878 \]

\[ (\text{O}_2\text{NOCH}_2\text{CHCH}_2\text{OCH}_2)_2\text{CH}_2\text{ONO}_2 \]

\[ \text{ONO}_2 \]

\[ \text{CH}_2\text{ONO}_2 \]

at 20°. It is prepd by the hydroxylation of PE diallyl ether (see above) with 3% H peroxide, followed by nitration. Although the expl props of this compd have not been reported, from the combination of high mw and low neg OB, it should be a good expl

Refs: 1) Beil 1(2817) 2) R. Evans & J.A. Gallaghan, JACS 75, 1248 (1953)

Written by C. H. McDonnell

Pentaerythritylamines

Monoamines. No deriv of pentaerythritylmonoamine (PE deriv in which one hydroxyl group has been replaced by an amino group) have been reported which are sens or expl

Diamines. Pentaerythritylamine [2,2-Bis (aminomethyl)-1,3-propanediol (name preferred by CA)]. \( \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2, \text{ mw } 134.18, \text{ hygroscopic crysts, prep by two steps from the} \)

\[ \text{CH}_2\text{NH}_2 \]

\[ \text{HOCH}_2\text{CHCH}_2\text{OH} \]

\[ \text{CH}_2\text{NH}_2 \]

diacetate ester of 2,2-bis(bromomethyl)-1,3-propanediol, yield 45.8%; and isolated as the dihydrochloride salt, mp 246-7° (Refs 1 & 3)

Dipicrate. \( \text{C}_6\text{H}_{14}\text{N}_2\text{O}_2,2\text{C}_6\text{H}_3\text{N}_3\text{O}_2, \text{ mw } 592.38, \text{ N } 24.1\%, \text{ OB to CO}_2 -75.7\%; \text{ golden yel ndls, mp } 223^\circ \text{ with decompn} \) (Refs 2 & 3)

Pentaerythritylmonoaminomonomide [3-Amino-2,2-bis(hydroxymethyl) propylguanidine (name preferred by CA)]. \( \text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_2, \text{ mw } 176.22, \text{ prep by the action of } \text{H}_2\text{NCSMe on} \)

\[ \text{CH}_2\text{OH} \]

\[ \text{NH} \]

\[ \text{H}_2\text{NCH}_2\text{HCH}_2\text{CH}_2\text{NH}_2 \]

\[ \text{CH}_2\text{OH} \]

PE diamine and isolated as the dinitrate salt, mp 128-9° (Ref 3)

Dipicrate. \( \text{C}_6\text{H}_{16}\text{N}_4\text{O}_2,2\text{C}_6\text{H}_3\text{N}_3\text{O}_2, \text{ mw } 582.43, \text{ N } 24.0\%, \text{ OB to CO}_2 -90.7\%; \text{ crys from Me alc, mp } 209.5-11.5^\circ \text{ with decompn} \) (Ref 3)

Pentaerythrityldeguanidine[1,1'-2,2-Bis(hydroxy-
methyltrimethylene diguanidine (name preferred by CA). C₂H₈N₆O₂, mw 218.26; prepd by the action of an excess of the nitrate salt of H₂NCSEt on PE diamine and isolated as the NH

\[
\text{CH₂OH} \quad \text{NH} \quad \text{CH₂OH}
\]

H₂NCSNHCH₂CH₂NHCSNH₂

Dinitrate salt, C₇H₁₈N₆O₄·2HNO₃, mw 344.30, N 32.5%, OB to CO₂ = -74.4%; mp 196°-8° with decom (Ref 3)

Dipicrate. C₇H₁₈N₆O₄·2C₆H₃N₃O₂, mw 676.47, N 24.8%, OB to CO₂ = -80.5%; a solid, mp 257°-9° with decom (Ref 3)

1,1'-(2,2-Bis( hydroxymethyl)trimethylene) bis (2-nitroguanidine). C₇H₁₆N₄O₆, mw 308.26, N 36.4%, OB to CO₂ = -83.1%; prepd by the

\[
\begin{align*}
\text{NNO₂} & \quad \text{CH₂OH} \quad \text{NNO₂} \\
\text{H₂NCSNHCH₂CH₂NHCSNH₂} & \quad \text{CH₂OH}
\end{align*}
\]

reaction of an excess of O₂NNCSEt on PE NH diamine, yield 26%, mp 200°-1° with decom (Ref 3)

1,1'-(2,2-Bis( hydroxymethyl)trimethylene) bis (2-nitroguanidine) Dinitrate. C₇H₁₄N₁₀O₁₀, mw 398.25, N 35.2%, OB to CO₂ = -44.2%;

\[
\begin{align*}
\text{NNO₂} & \quad \text{CH₂ONO₂} \quad \text{NNO₂} \\
\text{H₂NCSNHCH₂—CH₂NHCSNH₂} & \quad \text{CH₂ONO₂}
\end{align*}
\]
a crystal solid, prepd by the nitration of the above dihydroxy compd with 99% nitric ac, yield 85.5%; mp 158°-60° with decom (Ref 3)


Triamines. Pentaerythrityltriamine [3-Amino-2,2-bis(aminomethyl) propanol (name preferred by CA)]. C₅H₁₂N₃O, mw 133.19; prepd in CH₂NH₂ three steps from PE tetra-bromide and isolated as the hydrated tripicrate.

\[
\begin{align*}
\text{HOCH₂CH₂NH₂} & \quad \text{CH₂NH₂} \\
\text{C₅H₁₂N₃O.3C₆H₃N₃O₇} & \quad \text{C₅H₁₂N₃O₁.3C₆H₃N₃O₇}
\end{align*}
\]
mw 820.51, N 26.1%, OB to CO₂ = -70.2%; crys from w, mp 145° with decom (Refs 1 & 2)

Trinitrate. C₅H₁₄N₃O₃HNO₃, mw 322.23, N 26.1%, OB to CO₂ = -44.7%; mp 239° with decom (Refs 1 & 3)

Refs: 1) Beil 4, (809) 2) A. Litherland & F.C. Mann, JCS 1938, 1588 3) M. Bayaert & F. Govaert, Proc AcadSci Amsterdam 42, 776 (1939) & CA 34, 5414 (1940)

Pentaerythrityltetraakis(dichloramine) [N,N,N',N'-Tetrachloro-2,2-bis(dichloraminomethyl)-1,3-propanediamine (name preferred by CA)].

C₅H₁₂Cl₄N₄, mw 407.87, N 13.7%, OB to CO₂ & HCl = -39.2%; a solid, mp 54.0°-4.5°; prepd by

\[
\begin{align*}
\text{CH₂NCl₂} & \quad \text{CH₂NCl₂} \\
\text{Cl₂NCH₂CH₂NCl₂} & \quad \text{CH₂NCl₂}
\end{align*}
\]

the action of Cl (from NaOCl) on (PhCH·NCH₂)₄Cl. It decomps on standing above -15°, and the authors report it to be a powerful expl more sens than MF

Refs: 1) Beil, not found 2) E. Gryszkiewicz-Trochinowski et al, MP 40, 109 (1958) & CA 55, 2527 (1961)

Pentaerythrityltetraakis(nitramine) [Tetraakis(nitraminomethyl)methane, PETX]. C₅H₁₂N₈O₈, mw 312.20, N 35.9%, OB to CO₂ = -61.5%; colorl cryst, CH₃NHNNO₂

\[
\begin{align*}
\text{O₂NNHC₃CH₂NHNO₂} & \quad \text{CH₂NNO₂}
\end{align*}
\]

mp 175° with decom (Ref 4). It is prepd by the action of amm on (EtOOCCH₂)₄Cl NO₂

in w on a steam bath, yield 88% (Ref 4)

Explosive Properties. Explosion Temperature. Deflagrates at 295°

(Ref 2)

Heat Test at 120°. At 30 hours there was 32.4% wt loss and 35.6% decom (Ref 3)

Impact Sensitivity. Using the Bruceon No 3 app & a Skg wt, 27cm for 50% explns was obtained (RDX 48-50cm) (Ref 2)

International Heat Test at 75°. A zero wt loss was noted (Ref 2)

Power by Ballistic Mortar. 129% of TNT (Ref 2)
Thermal Stability at 100°. No acid fumes in 300 min (Ref 2); at 135° ignited in 240 min (Ref 2)

Vacuum Stability at 100°. 10.20cc of gas were evolved in 48 hours (Ref 2)


Pentaerythryltetraakis(trimethylammonium Bromide) ([(2,2-Bis(dimethylaminomethyl)trimethylene)bisp[trimethylammonium Bromide]], Dimethobromide [name preferred by CA]). C17H44Br4N4, mw 624.18; prep by heating
(CH2NMe3)4Br
Me3 NH2CH2CH2NHMe3
in a sealed tube a mixt of PE tetrabromide and trimethylamine in 95% Et alc for 18 hours at 230°, yield 72% (Refs 1 & 3)

Tetraperscholate. C17H44N44+4.ClO4−, mw 560.55, N 10.0%, OB to CO2 & HCl –108.4%; crystals from dil perchloric acid, decomps explosively at 380° (Refs 1 & 3)

Tetrapicrate. C17H44N44+4.C6H2N3O7−, mw 1217.0, N 18.4%, OB to CO2 –105.2%; yel crystals, mp 310° with decompn (Refs 2 & 3)

Refs: 1) Beil 4, (634) 2) Beil 6, (942) 3) F. Govaert & J. Cazier, NatuurwTijdschr 23, 149 (1942) & CA 37, 6245 (1943)

Pentaerythryltetraakis{2-aminoethylamine) [N,N’-Bis[2-aminoethyl]-2,2-bis[2-aminoethylamino]methyl-1,3-propanediamine] (name preferred by CA)]. C13H38N8, mw 304.48, N 36.8%; a light yel oil, bp 265–75° at 18mm;

CH2NHCH2CH2NH2
H2NCH2CH2NHCH2CH2NHCH2CH2NH2
CH2NHCH2CH2NH2
prepd by the action of an excess of ethylenediamine on PE tetrabromide and obtained as a hydrate (Refs 1 & 3)

Octapicrater. C13H36N8.8C6H3N3O7, mw 2137.4, N 36.8%, OB to CO2 –71.9%; a yel amorphous solid; mp, softens and decomps betw 120 and 160° (Refs 2 & 3)

Refs: 1) Beil 4, (635) 2) Beil 6, (942) 3) J. vanAlphen, Rec 57, 265 (1938) & CA 32, 4546 (1938)

Tetramines. Pentaerythryltetramine[2,2-Bis(aminomethyl)-1,3-propanediamine] (name preferred by CA)]. C5H16N4, mw 132.19. It is
CH2NH2
H2NCH2CH2NH2
CH2NH2
prepd by the action of ammonia in Et alc on PE tetrabromide (Refs 1, 3 & 5), or better by the action of p-toluenesulfonylmide on the same bromide followed by hydrolysis of the tetrasulfonate (Ref 4)

Tetranitrate. C5H16N4.4HNO3, mw 384.26, N 29.2%, OB to CO2 –50.0%; ndls, mp 220–2° with decompn, decomps explosively on rapid heating (Refs 1 & 7)

Tetranitroform Salt. C5H16N4.4HC(NO2)3, mw 736.35, N 30.4%, OB to CO2 –8.7%. It is prepd by the action of nitroform on the amine in 20% ac Et alc. The differential thermal analysis (DTA) thermogram shows a decomp exotherm at 90° (Ref 6)

Tetraperscholate. C5H16N4.4HClO4, mw 534.03, N 10.5%, OB to CO & HCl –6.0%. It is prepd by the action of ac perchloric acid on the tetramine in w. The DTA thermogram shows no mp, but a decomp exotherm at 246.5° (Ref 6)

Tetrapicrate. C5H16N4.4C6H3N3O7, mw 1048.6, N 21.4%, OB to CO2 –50.0%; ndls, prepd by the action of excess Na picrate on the
amine in w and isolated as a hydrate which can be dehydrated in vacuo; mp of hydrate 196–7° with decompn (Refs 2 & 4), of the anhydrous salt 206–8° (Ref 5)

Written by C. H. McDonnell


Pentaglycerol. See M116-R & M120-R in this Vol

Pentaglycerin Trinitramine. See M117-L in this Vol

Pentaglycerin Trinitrate. See M117-L & M120-R in this Vol

Pentaglycol. See Vol 5, D1357-R

Pentaglycol Dinitramine. See Vol 5, D1369-R

Pentaglycol Dinitrate. See Vol 5, D1358-L

n-Pentane. CH₃(CH₂)₃CH₃; mw 72.15; colorless liquid; mp -129.72°; bp 36.07°; d 0.6262g/cc at 20/4°; Rf 1.35748. Sol in acet, benz, chlf, ethanol, eth and heptane. V sl sol in w. The compd was first isolated in 1863 by Pelouze and Cahors from American petroleum. Synthetic prep is by treating 1,4-dibromopentane with Zn dust in 75% ethanol (Ref 2); however, the usual commercial method is by fractional distn of petroleum followed by purification by rectification (Ref 4). Lab prep consists of redn of an alkyl halide such as 2-bromopentane with Mg in an acid medium (Refs 5 & 21)

n-Pentane has a Qc of 19339 Btu/lb; its deton limits and initiation temp in chlorine are 2.42–43% and 20–2°, in oxygen 1.4–8.0% and 20–2°; a closed cup flash pt of -49°; an ign temp of 330°; and a visc of 0.279 centipoises at 0° (Refs 7–12 & 14–20)

Toxicity. Max allowable concn for an 8 hr exposure is 1000ppm or 2950mg/m of air. Higher concns produce a narcotic effect and eventual asphyxiation (Refs 16a & 22)

Uses. n-Pentane has found use as an anesthetic; an expl suppressant when mixed with a halogenated hydrocarbon and included in aircraft fuel (Ref 13); a jet engine fuel (Ref 16a); as a base for synthetic rubbers and plastics; a parent compd for the formation of nitropentanes and azido nitro pentanes used as expls and propelants (Refs 15a, 15b & 21a); also, as a parent compd for fluorine-contg resin binders which impart both thermal stability and, in conjunction with metal hydrides, high impulse to solid propelants (Ref 15b)


3,3-Diazido-2,4-Dinitrotolpentane. CH₃.CHNO₂.C(N₃)₂.CHONO₂.CH₃, mw 276.24; N 40.58%; OB to CO₂ -46.34%; white cryst; mp 64-60°, bp 135° (decomp); sol in benz and eth. Prepn is by first mixing acetic anhyd (10.68ccs) at 0-5° with 100% nitric acid (4.56cc) by dropwise addn of the acid. Solid diazidopentadiol (4.2g) is then added over a period of 20 min while maintaining the temp at 5-15°. Crystn occurs after 30 min of stirring. Pptn is completed by dourning the react mixt in ice-w. The prod is extrd with eth and recryst from hexane. The yield is 85%

The diazido cmpd can be detord by frction. It has an exp temp of 165°, a Qₐ of 825.4 (avg) kcal/mole; a Qₐ of 78.9 kcal/mole; and an impact sensy of 5.7cm using a 2kg wt and an Aberdeen Impact app with No 12 tools (vs 26.7cm for PETN). Theoretical calcs using the TIGER computer code determ the flame temp (3120°K), force (4.46 inch-lbs/b) and chamber press (39800 psi) of M-2 proplt when the diazido was substituted for NG in the formulation, (19.34%).

Another suggested application for the diazido nitrate cmpd is that of a combustible percussion primer for caseless ammo

Mononitropentanes, C₅H₁₁NO₂. The only cmpd of expl interest here is 2-Nitropropane which can be used as a rocket fuel constituent (Ref 3):

2-Nitropropane. CH₃.CHNO₂.CH₂.CH₂.CH₃, mw 117.18, N 13.60%, OB to CO₂ -184.33%, colorl oil, bp 148-50°, 0.938g/cc at 25/4°, RI 1.4092 at 25°. Soln in aq NaOH. Prepn is by reacting at 0° with stirring an ethereal soln of 2-nitroprop-1-ene with ethylmagnesium bromide, which is added v slowly. An additional hr of stirring at 20° is reqd to complete the reaction. Subsequent decompn of the Mg complex is obtbd by cautious addn of aq acetic acid. The cmpd is purified by steam distn, washing with aq sodium hydrogen sulftte, drying, and then fractionization

Dinitropentanes. C₅H₁₀(NO₂)₂, mw 162.15, N 17.21%, OB to CO₂ -108.5%. There is only one cmpd that is of expl interest here.

1,5-Dinitropentane. O₂N CH₂.CH₂.CH₂.CH₂.CH₃ NO₂, colorl oil, bp 134° at 1.2mm; RI 1.461. Soln in benz. Prepn is by reacting 1,5-diodopentane with Ag nitrite in eth. Its dисodium salt is v ltr sol in ethanol, and explds weakly when heated
Refs: 1) Beil 1, (350) 2) ChemRubHdb (1975), C-409

Alkyl substituted dinitropentanes. There are two such cmpds of interest:

1,2-Dinitro-2-Methyl-Propane. See Vol 5, D1991-R and Vol 2, B368-R where it is descbrd as Dinitro-isoo-butane

The Sodium salt of 1,1-Dinitro-2-Methoxy-Pentane. CH₃.CH₂.CH₂.CH₂.CH(OCH₃)₂.C(Na)(NO₂)₂, mw 142.15, yel ndls, mp, explds. Prepn is by slow (drop by drop) addn of Na methyl alco-
holate (2.3g Na/25cc of methanol) to 9.7g of 1-brom-1-nitro-1-amylene while cooling the reaction vessel with cold w. The salt is recryst from w. The compd expds on heating
Ref: J. Loew inich et al, Ber 63, 642 (1930) & CA, not found

Polynitropropanes. There are three compds of interest:

(±)-1,1,1,3-Tetranitropentane.
CH₃CH₂CH(NO₂)₂CH₂C(NO₂)₃, mw 252.21, N 22.22%, OB to CO₂ -38.06%, color: cryst, mp 240-0.5°, bp 112° at 0.2mm, d 1.4656 g/cc at 25/4°, RI 1.4712 at 25°. Sol in hexane. It is described in Russ lit as a tautomeric compd obtd from urea dissolved in methanol and re-acted with the aci form described next. The Tetranitro compd can be detond

1,1-Trinitro-3-acyl nitro Pentane.
CH₃CH₂C(OH)NO₂CH₂C(NO₂)₃; mp 70.5-71° (decomp). Prepd by reacting 2-Nitrobutene-1 with trinitromethane
Ref: Beil 1, (319)

1,1,1,3,5,5,5-Heptanitropentane.
(O₂N)₂C₃H₇(NO₂)₂CH₂C(NO₂)₃, mw 387.24, N 25.33%, OB to CO₂ -26.86%, white cryst, mp 104° (decomp), d 1.74g/cc. Sol in acet, eth, chlf, ethanol, dinitrobutyl acrylate and toluene. Vls sol in w. Prepn is by dropwise addn of a cold soln of 7.5g of nitroallyl acetate in 20cc of methanol over a period of 60 mins, to a continuously stirred mixt which is maintained at 0° of 15.1g of nitroform in 150cc of w, using 1 ml of a 20%aq soln of NaOH as the catalyst for the reaction. The prod is first w-washed and then recrystd from 70% nitric acid at 75°. The 66% recryst yield is then dessicator dried

The exp has a Qₜ of 1560cal/g (avg) using w at 25° as ref, a negligible hygroscopicity; an ign temp of 196°; an impact sensy of 65-70cm at the 50% pt using a BM app with a 2kg wt (PETN ref is 26-8cm); power by Ball in t is 143 (150 for RDX ref); power by Trauzl test is 181 (157 for RDX ref); a thermal stability at 65.5° of failure after 25 min using KI-starch indicator paper; a thermal stability at 134.5° of failure after 4 min (charred residue after 5 hrs) using methyl violet indicator paper; a storage stability of several weeks at RT; and a vac stability of 6.1cc of gas/g at 90° in 48 hrs


Iso-Pentane or 2-Methylbutane (called Isopentan or Dimethylallyl methyl by Beil).
(CH₃)₂CH.CH₂.CH₂; mw 72.15, color: liq, mp -159.9°, bp 27.8°, d 0.6201g/cc at 20/4°, RI 1.35370. Sol in ethanol, ether, hydrocarbons and oils, insol in w. First prepd by Frankland in 1850 by treating iso-amyl iodide with Zn in w at 140° (Ref 2). It was isolated by Young from American petroleum (Ref 3). Present methods of prepn include fractional distn of petroleum and subsequent purification of the crude isopentane by rectification, as well as cracking and reforming of crude oil components and natural gasolines in oil refineries (Refs 4 & 7)

Isopentane has expl limits in air of 1.4 to 7.6% and a closed cup flash pt of -51° (Refs 5 & 7). It can be nitrated in the vapor phase, but these derivs have not been used as expls (Refs 1 & 6)


Pentanitrocellulose. See Vol 2, C100-R

Pentanitroaniline (PNA). See Vol 1, A414-L

Pentanitroazobenzene. See Vol 1, A649

Pentanitrobenzocarbazole. See Vol 2, B66-R
Pentanitrodiethylenediamine. See Vol 5, D1247-R

Pentanitrodimethylaminodiphenylamine. See Vol 5, D1310-L

Pentanitrodimethylaniline. See Vol 5, D1316-L

Pentanitrodimethyl-m-phenylenediamine. See Vol 5, D1363-R

Pentanitrodiphenylamine. See Vol 5, D1434-R

Pentanitrodiphenylethanol. See Vol 5, D1459-L

Pentanitrodiphenylether. See Vol 5, D1453-L & R

Pentanitrodiphenylsulfide. See Vol 5, D1477-R

Pentanitrodiphenylsulfone. See Vol 5, D1480-L

Pentanitroethylaniline. See Vol 6, E207-R

Pentanitromethylaniline. See in this Vol, M101-R

Pentanitronaphthol. See this Vol, N20-R

Pentanitrophenyl/methylene/trimine. See this Vol, M102-R


3-Pentanone (Propionone, Diethylketone or DEK). CH₃(CH₂)₂.CH₂.CH₃; mw 86.13; color lq; mp –39.8°; bp 101.7°; d 0.8138 g/cc at 20/4°; RI 1.3924. V sol in w; sol in ethanol and acet. Prepn is by the dehydration of 3-pentanol using copper-chromium oxide as a catalyst at 275–300°. Other methods of prepn are listed in Beil. DEK has a lower expl limit of 1.6% in air and a closed cup flash pt of 13° (Ref 3) Refs: 1) Beil 1, 679, (351), [738], [806] & [3279] 2) I. Mellan, “Ketones”, Chem Pub, NY (1968), 94 3) L. Bretherick, “Handbook of Reactive Chemical Hazards”, CRC Press, Cleveland (1975), 451 4) ChemRubHdb (1975), C-414

Pentastit. Trade name for Swiss military expls prepd by phlegmatizing PETN with pentaerythritol tetraurate (called pentaerythrit-tetraurate in Ger). These expls were manufd by the Schweizerische Sprengstoff Fabrik AG at Dottikon, Switzerland. The properties and comps of some Pentastit expls, with and without Al are reported as follows:
<table>
<thead>
<tr>
<th>Property</th>
<th>93/7 Pentastit</th>
<th>96.5/3.5 Pentastit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point, °C</td>
<td>137</td>
<td>138</td>
</tr>
<tr>
<td>Explosion temp. (20°C/minute, °C)</td>
<td>192</td>
<td>198</td>
</tr>
<tr>
<td>Impact sensitivity, 5 kg hammer, cm</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.56</td>
<td>1.60</td>
</tr>
<tr>
<td>Velocity of deton., meters/second</td>
<td>8000</td>
<td>8100</td>
</tr>
<tr>
<td>Trauzl test value, cc/10g sample</td>
<td>408</td>
<td>420</td>
</tr>
<tr>
<td>Copper cylinder compression test, mm</td>
<td>3.50</td>
<td>3.63</td>
</tr>
</tbody>
</table>

**Refs:** 1) Schweiz Sprengstoff-Fabrik AG, SwisSp 220756 (1942) & CA 42, 6538 (1948)  
2) Stettbacher (1948), 67 & 122–3  3) M. Freiwald, Explosivst 6, 133 (1961)

**Pentazenes (Pentazidienes).** These are derivatives of a compd cong five nitrogen in an open chain, such as RN:N.NR:N:N, where R stands for hydrogen, or an alkyl or aryl radical. These compds contain high percentages of nitrogen, and therefore release large volumes of gas on decompn. Listed below are representative examples of those reported to explode on heating, impact or friction.

In naming the derivatives of pentazes, the numeration of the nitrogens of the open chain is in **Roman numerals, I, II, III, IV and V**: the numeration of any substituent attached to the nitrogens is in **Arabic numerals**

**I,V-Diphenyl-pentazide.** (called 1,5-Diphenyl-pentazidien-1,4) or Bis(diazobenzolamid by Beilstein). C₁₂H₁₁N₂:N.NH₂:N.C₆H₅, mw 225.25, N 31.09%, yel prisms, mp explds. Was prepd by Griess (Ref 2) by adding a cold satd aq soln of benzenediazonium nitrate to ammonia. Insol in w, sol in alc and eth with decompn. In the dry state, it explds violently when heated, or on impact or friction

**Refs:** 1) Beil 16, 753  2) P. Griess, Ann 137, 81 (1866)  3) H. von Pechmann & L. Frobenius, Ber 27, 898–9 (1894); 28, 171 (1895)

**I,III-Diphenyl,V-tolyl pentazen.** [Called 1,3-Diphenyl-p-tolyl-pentazidien-1,4) or Benzoldiazio-p-toluoldiazoonil by Beilstein; Diazobenzol-p-diazotoluolanilid by von Pechmann]. C₁₀H₁₁N₂:N.N(C₆H₄ CH₃)₂:N.N(C₆H₄ CH₃)₂, mw 315.37, N 22.21%, yel needles, mp (explds at about 72–73°). Can be prepd from diazoaminobenzene and p-toluenediazonium chloride in the presence of Na methylate in methanol. Insol in w, sol in alc. Explds on heating

**Refs:** 1) Beil 16, 754  2) H. von Pechmann & L. Frobenius, Ber 28, 171 (1895)

**I,V(Di-4-tolyl),3-ethyl pentazen.** [Called 3-Aethyl-1,5-di-p-tolyl-pentazidien-1,4) or Bis-p-toluoldiazo-athyramid by Beilstein]. (CH₃C₂H₅)₂N:N.N(C₆H₄ CH₃)₂:N.N(C₆H₄ CH₃)₂, mw 281.35, N 24.89%, pale yel needles from ligr, mp 121° (with violent evolution of gas). Was prepd from p-toluene diazonium chloride and ethylamine. Easily sol in eth and benz, more difficultly in alc and ligr

**Refs:** 1) Beil 16, 754  2) H. Goldschmidt & H. Holm, Ber 21, 1025 (1888)

**I,V-Di-4-tolyl pentazen.** Called Di-p-tolylpentazidien-1,4) by Beilstein; Bis-p-diazotoluolamid by von Pechmann). (CH₃C₂H₅)₂N:N.NH₂:N.N(C₆H₄ CH₃), mw 253.30, N 27.65%, needles, mp (deflagrates at 79–83°). Can be prepd by adding p-toluenediazonium chloride soln dropwise to an excess of ammonia at 0°. Deflagrates when heated; explds on impact or friction
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Refs: 1) Beil 16, 754  2) H. von Pechmann & L. Frobenius, Ber 27, 899 (1894)

[I & III-Di-4-tolyl, V-phenyl] pentazene. (Called 1-Phenyl-3,5-di-p-tolyl-pentazidien (1,4) or Benzo-
diazo-p-toluidol-diazo-p-toluidin by Beilstein; Diza-
obenzol-p-diazetoluolotoluidin (by Pechmann).
(CH₃C₆H₄)N::N(NC₆H₄CH₃):N::N:C₆H₅, mw 329.39, N 21.26%, yel needles, mp (explds at
76°). Can be prep'd by adding a methanolic
sln of benzoldiazonium chloride to a metha-
nolic sln of p,p'-diazaaminotoluol (Beil 16,
709) and Na methylate. Sol in acet. Explds on
heating
Refs: 1) Beil 16, 754  2) H. von Pechmann & L. Frobenius, Ber 28, 170 (1895)

[I,I,II,V-Triphenyl] pentazene. (Called 1,3,5-
Triphenyl-pentazidien (1,4) or Bis-benzoldia-
zanilin by Beilstein; Bisdiazobenzanilin or
Benzoldiazoanilindiazobenzol by von Pechmann).
C₆H₄:N::N(C₆H₄)N::N:C₆H₅, mw 301.34, N
23.24%, yel leaflets, mp (explds at 80–81°).
Can be prep'd by treating a methanolic sln of
2 moles of N-nitrosoacetanilide (Beil 12, 581)
with 1 mole of K methylate or ethylate. Diffi-
cultly sol in ac and eth, sol in acet, chlf and
benz. Explds on heating or light impact
Refs: 1) Beil 16, 753  2) H. von Pechmann & L. Frobenius, Ber 27, 703–4 (1894)

[I,I,II,V-Tri-4-tolyl] pentazene. (Called 1,3,5-
Tri-p-tolylpentazidien (1,4) or Bis-p-toluoldiazo-
p-toluidin by Beilstein; Bis-p-diazetoluol-p-toluid
by von Pechmann).
(CH₃C₆H₄)N::N(NC₆H₄CH₃):N::N(C₆H₄CH₃),
mw 343.42, N 20.39%, yel needles, mp (defla-
grates at 88°). Can be prep'd by adding metha-
nolic Na methylate to a methanolic sln of p-
toluidine, followed by methanolic p-toluene-
diazenium chloride. Difficultly sol in ac, eth
or lgr; easily sol in chlf and benz. Explds on
heating or on strong impact
Refs: 1) Beil 16, 754  2) H. von Pechmann & L. Frobenius, Ber 27, 705 (1894)  3) E. Bam-
berger, Ber 27, 2597 (1894)

Pentek. A proprietary trade name for a mixt
of approx 88% pentaerythritol (PE) and 12%
related polyhydric alcohols, mostly dipenta-
erythritol (DPE). It is prep'd in the same manner
as PE, starting with acetalddehyde, formaldehyde
and alkali, except that the purification pro-
dure is more simple. This mixt has found ex-
tensive use in the protective coating industry
and in the manuf of synthetic drying oils. It can
also be used (price permitting) for the prep
of a commercial expl which would consist
chiefly of Pentaerythritol tetranitrate (PETN),
the balance being Dipentaerythritol hexanitrate
(DPEHN), Tri-pentaerythritol octanitrate
(TPEON), Tetrapentaerythritol decanitrate
(TePEDeN), nitrated forms of PE, etc
Ref: T.M. O'Neil, PaintIndMag 62, 370–84
(1947) & CA 42, 1065 (1948) (Correction in CA
42, 5686 (1948))

Penthritins (Swiss). See Vol 3, C443-R and
Vol 6, G51-L & 52 (Table G17)

Pentrite, Pentrit. Same as Pentaerythritol
Tetranitrate (PETN)

Pentofive. Expl contg PETN 50, Fivenolite 50%
(see Vol 6, F41)
Ref: D.P. MacDougall et al, OSRD 5744, 5745 &
5746 (1945)

PENTOLITES

Pentolites are castable expl mixts containing
PETN and TNT. The most commonly used
blend consists of 50/50 PETN/TNT, but other
blends such as 75/25, 40/60, 30/70 and 10/90
have been occasionally employed. Molten TNT
dissolves appreciable amounts of PETN as shown
in Fig 1. The eutectic in the TNT-PETN system
occurs at 76.7° for a 87/13 TNT/PETN mixt.
Because correspondingly more PETN than
RDX dissolves in TNT, the viscosity of Pento-
lites at casting temperatures is less than that of
comparable Cyclotolts (RDX/TNT blends)
The cast density of Pentolites does not vary appreciably with blend compn. 50/50 Pentolite (hereafter to be referred to simply as Pentolite) has a cast density of 1.63–1.67g/cc (Ref 8a), while 10/90 Pentolite has a cast density of 1.60 g/cc (Ref 12). The density of pressed Pentolite lies between 1.60 and 1.65g/cc. Since Pentolites are blends (no compound formation) they are soluble in the same solvents as their constituents (PETN & TNT). Pentolite has a compressive strength of 2000–2200psi at 1.68g/cc (Ref 12).

Boyle et al (Ref 7b) give a Hugoniot for "unreacted" Pentolite of 1.67g/cc in the form of U=2.83+1.91u where U is the shock velocity and u is the particle velocity.

Uses. During WWII cast Pentolite was used as the main charge in hand and anti-tank grenades and as a pressed charge in some detonators (Ref 8a). Currently it still finds limited use in boosters and primer charges in commercial blasting.

Casting is usually accomplished at around 90°. Constant stirring is required to keep the PETN suspended as only about 20% PETN dissolves at this temp. It is desirable to use small elongated PETN crystals to minimize settling of the PETN, thus preventing the production of non-uniform charges. W.O. Williamson (Ref 4) claims that in 50/50 Pentolites cast at 90–4°, PETN crystals retain their original shape characteristics, since little soln occurs at such temps. These crystals were enclosed by cryst TNT. Added wax caused no obvious changes in the microstructures, and at least some persisted as segregations. Microstructures resembled those of TNT.

Pressing. The same methods as used in the press-loading of Amatols (see Vol 1, A160–61) can be used for Pentolites.

Specification. JAN-P-408 (1946) contains the following general requirements for Pentolite: Volatile matter: 0.5% max; Composition: 50 ± 2% TNT; Total acetone insol: 0.04% max; Inorganic acetone insol: 0.02% max; Acidity or Alkalinity: 0.005% max; Grit: non; PETN granulation: thru No 30 sieve, 95% min; thru No 200 sieve 30% max; and Stability: not more than 5ml of gas in 100° heat test.

Preparation. Two methods have been used in large scale Pentolite production. In the more modern slurry method, PETN in water is stirred and heated above 80°, and then TNT is added. The molten TNT coats the PETN particles. The resulting slurry is cooled under rapid stirring, and the separated granules are filtered out and dried at below 75°. In the coprecipitation method, PETN and TNT are dissolved separately in acet and the solns are then mixed. The Pentolite is pptd by pouring the mixed solns into cold water using vigorous agitation. After filtering, the Pentolite is air dried (Ref 12). The slurry method permits better particle size control than the coprecipitation method. It is also more economical of acet (acet is used in the slurry method for obtaining PETN of the desired particle size), and takes less time per complete production cycle.

Explosive Properties (50/50 blend). Ref 12
gives the following expl properties for Pentolite:
OB to CO₂ –42%; Detonation velocity 7465 m/sec at d 1.66g/cc in one-inch diameter; Ballistic mortar 126% TNT; Trauzli test 122% TNT; Impact sensitivity (2kg wt) 34cm in BuMine App and 12 inches in PicArsn App; Friction pendulum – unaffected; Explosion temp 0.1 sec at 290° and 1 sec at 266°.

Dobratz (Ref 13) summarizes other Pentolite properties as follows: Detonation Velocity (D) = 7470m/sec at d 1.67g/cc, and ΔD/ΔT = −0.4 x 10⁻³ (mm/microsec °C); Small scale LASL gap test (50% thickness for brass spacers), 105–140 mls at 1.68g/cc and 32–38 mls at 1.70g/cc; Measured ΔHdet = 1.23kcal/g and ΔH² = −23.4kcal/mole; Calc ΔHdet = 1.41kcal/g; Theoretical max density, 1.71g/cc; Vapor press, 0.1 mm Hg at 100°C.

Cook (Ref 4a, pp 45 and 48) gives the variation of D with packing density ρ as: D = 5480 + 3100 (ρ–1.0) in m/sec, and shows that “ideal” D is attained for one-inch diameter charges.

Jameson & Hawkins give the CJ pressure of Pentolite as 245 × 10kbar (Ref 10a).

Shear (Ref 6) quotes an expl CJ pressure, obtained by Gehring & Dewey, of 237kbar, and D = 7620m/sec at d 1.66g/cc.

Figures 2 and 3 show Urbanski’s data (Ref 1) for the expln properties of low density Pentolite charges as a function of the PETN/TNT compn.

Dobratz (Ref 13) lists a computed CJ pressure of 250kbar at d 1.66g/cc and a polytropic exponent (γ) of 2.73. Theoretical computations by Shear (Ref 6) give CJ pressure (232kbar), detonation product compn, and isentropic expansion for Pentolite.

Macek (Ref 5) used Pentolite (and DINA) to study the transition from deflagration to detonation (DDT). He found that in Pentolite, heavily confined and ignited by a hot wire, a low-velocity regime (1–2mm/microsec) precedes steady detonation for 30–80microsec. Compression waves precede the burning front in this pre-detonation region and appear to coalesce into a shock wave.

Obmenin et al (Ref 10b) found LVD (low velocity detonation) at 1000–2000m/sec in cast Pentolite enclosed in 3mm ID steel tubes whose wall thickness was varied from 1.3 to 17mm. LVD was initiated by an igniter pin at the closed end of the tube and propagated for about 15 to 40 charge diameters. Tube-wall thickness increased the LVD value up to a wall thickness of 8mm. Above 8mm, LVD was independent of tube thickness.

UraKawa and Masutomi (Ref 8a) studied the heat stability of Pentolite using gas chromato-
graphy and DTA. Slow decomps starts at 110\(^\circ\) and is followed by the main pyrolysis reactions which generate NO\(_2\) rapidly. The rate of pyrolysis of the mixt (ie, the Pentolite) is faster than that of either TNT or PETN

Pentolite at d 1.56g/cc is used as the standard donor charge in the NOL "Large Scale Gap Test" (Ref 10)

Pentolite is also used as a standard charge for both air blast and underwater blast measurements. Extensive air blast measurements using Pentolite were made by Stoner & Bleakney (Ref 3). Theoretical air blast computations for Pentolite (and TNT) have been given by Shear & Wright (Ref 7) and by Shear (Ref 7a)

Underwater blast effects for Pentolite are given by Cole (Ref 2). Recent peak pressure measurements (Ref 9) confirm Cole's results. Cole (Ref 2) gives the following equations for the underwater shock effects of Pentolite at 1.6 g/cc:

\[
\begin{align*}
\text{Peak pressure} & = 2.25 \times 10^4 \left(\frac{W^{1/3}}{R}\right)^{1.13} \text{ psi} \\
\text{Impulse} & = 2.18 \frac{W^{1/3}}{R^{1.02}} \text{ psi-sec} \\
\text{Energy} & = 3.27 \times 10^2 \left(\frac{W^{1/3}}{R^{2.12}}\right) \text{ inch-lb/inch}^2
\end{align*}
\]

where W is the charge weight in lbs and R is the distance, in feet, from the center of a spherical charge

Olenko & Parshiev have computed the ratio of underwater shock energy of Pentolite to its total chemical energy to be 0.57 to 0.59 (Ref 8)

Nomograms for obtaining both air and underwater blast effects for Pentolite (and other explosives) are given in Navord 2986 (1955)

Sternberg & Walker (Ref 11) calc the flow following the detonation of a centrally initiated Pentolite sphere in fresh water at sea level, up to the time the main shock in the water is 100 charge radii from the center. Pressure, particle velocity, and temp vs distance at various times are obtained; also peak pressures, time constants, and pressure vs time at fixed positions. Partial steam formation in the water close to the gas bubble is shown to be possible but unimportant at the distances covered. The partition and distribution of kinetic and internal energies in the water and the gas sphere, and the energy dissipated by shock heating are found. The calc dissipated energy is 33% of the total energy released in the detonation when the shock front is 10 charge radii from the center, and 40.5% when the distance is 100 charge radii.


Pentonal. Exp contg PETN 47, TNT 33 & Al powder 20%
Ref: D.P. MacDougall, OSRD 5744, OSRD 5745 (1945)

Pentalite or Tetralite. Same as Pentanitromethylaniline (See in this Vol, M101-R to M102-L)

Pentrients. Same as Penthrinites

Pentrit or Penta (Swiss). Same as Pentacrylthritol Tetranitrate (PETN)
Pentritol. Same as Pentolite, according to Stettbacher, NC 11, 63-7 (1940)

Pentryl. Same as 2-(2',4',6'-Trinitro-n-nitraminolino)-ethanol nitrate. See Vol 1, A425-L to A429-R.

Pentryl and Pentro. Trade names for Swiss military expls cong mixts of PETN and TNT in various proportions. They are prep’d by dissolving PETN and TNT in acetone and precipitating them with water. They are manufd by the Schweizerische Sprengstoff-Fabrik AG, Dottikon, Switzerland.

The properties & comps of some Pentryl expls, with and without Al, are reported as below

Note: 70/30 Pentryl contains 70% PETN and 30% TNT. See also under Swiss Commercial Explosives of Nonpermisssible Type in Vol 3, C443-R

Refs: 1) Stettbacher (1948), 123 2) B.T. Fedoroff, private communication with A. Stettbacher, Dec 14, 1953

Pentyl. Swedish name coined by the Bofors Co in the 1930’s for PETN, because the Ger name “Nitropenta” used at that time was not considered suitable

Ref: B.T. Fedoroff, Private communication with C.M. vonArbin of the Bofors Co (March 6, 1963)

70/30 Pentryl

<table>
<thead>
<tr>
<th>100%</th>
<th>15% Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>70-130</td>
<td>70-130</td>
</tr>
</tbody>
</table>

Explosion temp (20°C/minute), °C

| 202  | 202 |

Impact sensitivity, 5-kg hammer, cm

| 23   | 22  |

Density, g/cc

| 1.58 | 1.65 |

Velocity of detonation, meters/second

| 7800 | 7400 |

Trauzl test value, cc/10g sample

| 394  | 498  |

Copper cylinder compression test, mm

| 3.48 | 3.49 |

PEP-3. One of the US plastic high expls developed during WWII, consisting of PETN 86 and Gulf Crown E Oil 14%. Its sensitivity, stability and performance properties are detailed below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cc</td>
<td>1.47</td>
</tr>
<tr>
<td>Explosion Temp, °C</td>
<td>257</td>
</tr>
<tr>
<td>Impact Test, 2kg wt.</td>
<td></td>
</tr>
<tr>
<td>BM App, cm</td>
<td>92</td>
</tr>
<tr>
<td>PicArsn App, inches</td>
<td>10-12</td>
</tr>
<tr>
<td>Ballistic Mortar Test, TNT equiv.</td>
<td>118</td>
</tr>
<tr>
<td>Hygroscopicity (90% RH, 30°)</td>
<td></td>
</tr>
<tr>
<td>% Gain in wt in 200 hours</td>
<td>0.04</td>
</tr>
<tr>
<td>Pendulum Friction Test, Steel Shoe.</td>
<td></td>
</tr>
<tr>
<td>Number of trials</td>
<td>10</td>
</tr>
<tr>
<td>Unaffected</td>
<td>10</td>
</tr>
<tr>
<td>Plate Dent Test</td>
<td></td>
</tr>
<tr>
<td>Block (Engineer Corps Special Blasting Cap used for initiation), dent, inches</td>
<td>0.109</td>
</tr>
<tr>
<td>Cylinder (35g Tetryl Booster plus Engineer Corps Special Blasting Cap used for initiation), dent, inches</td>
<td>0.215</td>
</tr>
<tr>
<td>Rate of Detonation, m/sec</td>
<td>7780 (d 1.47g/cc)</td>
</tr>
<tr>
<td>TNT at d 1.60g/cc</td>
<td>6795</td>
</tr>
</tbody>
</table>
Rifle Bullet Impact Test.

Number Trials 5
Partial Detonation 0
Burned 0
Unaffected 5

$100^\circ$ Heat Test.

% Loss in 1st 48 hrs 0.06
% Loss in 2nd 48 hrs None
Explosion in 100 hrs None

Sand Test.

Sand Crushed, g (TNT=44.1) 46.8

$100^\circ$ Vacuum Stability Test.

CC gas in 40 hrs 0.32–0.48

$120^\circ$ Vacuum Stability Test.

CC gas in 40 hrs 11+

PEP-3 did not possess the important property of remaining essentially unchanged in physical characteristics over a $-65^\circ$F to $+169^\circ$F temp range. It did not remain plastic at $-65^\circ$F, and exuded badly at only slightly elevated temps. The residue left by this exudation was markedly more sensitive than the original expl. It was concluded that plastic expl PEP-3 did not have sufficiently promising characteristics to warrant attempted improvement by modification (Ref 1)

Refs: 1) S. Livingston & S. Fleischnick, PATR 1696 (1948) 2) L.H. Eriksen & R.C. Grass, PATR 1713 (1949)

Pepperbox. A firearm with a cluster of barrels, often a revolver, each barrel of which fires separately. Some weapons with fixed barrels and rotating hammers may also be classed as pepperboxes


Peracids, Organic (Peroxy Acids). See Peroxides.

Organic of Structure RC(=O)OOH

Perafex. An Allied mechanical deception device produced during WWII. They would be dropped from the air and, on hitting the ground, would imitate the sound of rifle fire and the expln of hand grenades


Peragon. See under Paragon in this Vol

Peralite. Large grain proplnt contg K nitrate 63, charcoal 30 and Sb sulfide 7%

Ref: Daniel (1902), 604

Perammons. See under Parammons in this Vol

Percarbonates. Salts of the hypothetical percarboxylic acid, $\text{H}_2\text{C}_2\text{O}_6$, contg the $\text{C}_2\text{O}_6^{2-}$ radical, some of which are expl. Guided by analogy with persulfates, Constam and von Hansen (Refs 1 & 2) prepd several percarbonates by electrolysis of aq solns of corresponding carbonates, maintained at low temp. For details of the procedure, see Mellor (Ref 2)

Note: According to Mellor (Ref 2, p 86), A. Bach claimed that percarbonic acid can exist in cold ethereal soln. When such a soln was treated with an alc KOH soln, a bluish-white ppt of K percarbonate was formed. Of the percarbonates, the K salt is the easiest to prepare and is available commercially (see below)

Refs: 1) E.J. Constam & A. von Hansen, Zeit-Electrochem 3, 137 (1897) & GerP 91612 (1896) 2) Mellor 6 (1925), 82–87 3) Hackh’s (1972), 498-L

Potassium Percarbonate. $\text{K}_2\text{C}_2\text{O}_6\cdot\text{H}_2\text{O}$, mw 216.23; white, granular mass; mp 200–300º. Was first prepd in 1896 by E.J. Constam & A. von Hansen (Ref 2, p 85) by the electrolysis of a concd aq soln of K carbonate, cooled to $-15^\circ$.

A more modern prepn of practically anhyd cmpd is reported by Partington et al (Ref 3)

K percarbonate is sparingly sol in alc; it dissolves in ice cold w almost without decomp, but at RT and higher, it decomp with the evolution of $\text{H}_2$. 

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A percarbonate possesses, according to Daniel (Ref 1), some expl properties because it can be detonated if a sufficiently powerful detonator is used. According to Mellor (Ref 2, p 86), a violent reaction took place when a soln of 0.5g of solid phosphoric acid, some ether, and a few drops of w were added to 2g of K percarbonate. It was used by Turpin in Fr in expl mixts, ie, "Pyridyalutes" (qy) (Ref 1)

K percarbonate is highly toxic, and a strong irritant to tissue. It is also a fire risk in contact with organic materials (Refs 4 & 5)

Refs: 1) Daniel (1902), 778 (under Turpin)
2) Mellor 6 (1925), 82-87
4) Merck (1968), 856-L
5) CondChemDict (1971), 724-L
6) Hackth's (1972), 541-L

Perchlorates. See under Perchloric Acid and Perchlorates

Perchloratits or Perchloratites. Industrial blasting expls, based on perchlorates, used in Ger before and after WWI. Naoûm (Refs 1 & 2) lists the comps shown in Table 1:

<table>
<thead>
<tr>
<th>Ingredients:</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K perchlorate, of which up to 10% of the total expl may be replaced with Am nitrate and/or K nitrate</td>
<td>60-75 62-75</td>
</tr>
<tr>
<td>K and/or Am perchlorate</td>
<td>30-40</td>
</tr>
<tr>
<td>Am nitrate</td>
<td>35-45</td>
</tr>
</tbody>
</table>

Note: When Am perchlorate is incorporated some of the Am nitrate is replaced by K nitrate in an amt chemically equiv to the amount of Am perchlorate.

| Vegetable meal                                   | 1-5            |
| Vegetable meal and/or solid hydrocarbon          | 1-8 3-8        |
| Nitroglycerin (ungelatinized)                    | 3-6            |
| Nitroderivatives of toluene and/or napthalene and/or diphenylamine in which up to 4% of the total expl may be substituted with NC | 20-30 20-30 15-20 |

Stettbacher (Ref 3) details the Perchloratites listed in Table 2:

<table>
<thead>
<tr>
<th>Perchloratites:</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K perchlorate</td>
<td>68 35 34</td>
</tr>
<tr>
<td>Am nitrate</td>
<td>10 42 48</td>
</tr>
<tr>
<td>TNT and DNT</td>
<td>16</td>
</tr>
<tr>
<td>DNT</td>
<td>16</td>
</tr>
<tr>
<td>Wood (or vegetable) meal</td>
<td>1 5 6</td>
</tr>
<tr>
<td>NG (nitroglycerin)</td>
<td>4 4 -</td>
</tr>
<tr>
<td>MNN (mononitronaphthalene)</td>
<td>1 -</td>
</tr>
</tbody>
</table>

Refs: 1) Naoûm, Expls (1927), 134
2) Naoûm, NG (1928), 431
3) Stettbacher (1933), 316
4) Pepin-Lehalleur (1935), 347
5) Vivas, Felgenspan & Ladreda 2 (1946), 348
supply of surplus perchlorates were exhausted, the manuf of perchlorate expls was nearly discontinued because of the high cost of perchlorates from new sources
Refs: 1) Davis (1943), 364  2) PATR 2510 (1958), 129

PERCHLORIC ACID AND PERCHLORATES

Historical Introduction and Perchlorates in General History. The early history of perchlorates and the perchlorate industry has been thoroughly discussed (Refs 12 & 14, p 2), so it will be only briefly reviewed here. Early expnl work on perchlorates and perchlorates was closely tied to the discovery and identification of Cl. Several workers, notably Priestly, Lavoisier, and Scheele reported the isolation of volat hgs and gases which probably were oxides or oxoacids of Cl, but they failed to identify and characterize the compds isolated. Scheele, for example, treated muriatic ac (HCl) with Mn dioxide and obtained a volat liq which he called "muriatic ac derived of its phlogiston" (Ref 14, p3). The first perchlorate definitely identified was the K salt which was prepd by Stadion in 1816 by the decompn of K chloride (Ref 2). From this he prepd a hydrate of perchloric ac by heating the K salt with sulfuric ac (Ref 3). Pure (anhyd) perchloric ac was first prepd by Roscoe in 1862 by distn of the hydrated ac (Ref 4)

At present most perchlorate salts are prepd from Na perchlorate or perchloric ac by exch or displacement reactions (Ref 13, p4). Na perchlorate is prepd in two steps by the electrolysis of Na chloride; first to Na chloride, then in a second electrolysis to Na perchlorate (Ref 13, p 4)

General Information Valid for all Perchlorates. In perchloric ac and perchlorates the Cl is in its highest oxidn state. Hence they are good oxidizing agents and have been widely used in the expl, proplnt, and other 1nds for their oxidizing power. In addn, perchloric ac is a strong ac, pH of a 0.72M soln is 1.02 (Ref 7), and salts have been prepd from most metals as well as inorganic and organic bases (for individual compds see in the text below)

Analytical Procedures (general procedures use-

ful for the analysis of all perchlorates). For a review of procedures used prior to 1953 see Ref 9. 1) Qualitative. The presence of the perchlorate ion is best detd qualitatively by the addn of a 0.2%aq soln of methylene blue. A violet ppt forms which, when dried, deliquesces on heating (Ref 5). 2) Quantitative. The first effort to develop a gravimetric procedure for the detn of perchlorates was by Loebich who proposed the use of Nitron as a precipitant (for the structure of this reagent see Ref 10) (Ref 6). It was found that chlorides, chlorates, and nitrates interfere by forming insol ppts (Ref 6). Later it was found that w sol perchlorates could be analyzed gravimetrically by pptn of the perchlorate ion as tetraphenylarsonium perchlorate (Ksp at 20° = 2.60 ± 0.14 x 10^-9). The ppt can be dried at 105° and weighed directly (Ref 16). Still more recently a specific perchlorate ion electrode has been developed (Ref 17) which can be used for the potentiometric titration of the perchlorate ion using a soln of tetraphenyl-
arsonium chloride as the titrant (Ref 15). Tetraphenylphosphonium chloride has been similarly used, but the corresponding Sb compd is too insol in w for practical use (Ref 8). For routine assay of perchlorates for use by the armed forces, a Na carbonate fusion procedure is described in Mil Specs MIL-A-23946 (19 Aug 1964) & MIL-A-23948 (19 Aug 1964) (see also under Ammonium Perchlorate). The tetra-

phenylarsonium chloride procedure has also been proposed for use in Mil Specs (Ref 11)

Safety. As stated above, perchlorates are strong oxidizing agents and will react with reducing substances, with expl violence when hot (Ref 13). The impact sens of perchlorate salts depends to a great extent on the cation present. Metal perchlorates are relatively insolns; while organic perchlorates, particularly those in which the OB is close to 0, are extremely sens. For details see below under individual perchlorates
Refs: 1) Gmelin Syst No 6 (1927), 362; Supp B-2 (1969), 421  2) F. VonStadion, Gilbert's AnnPhys 52, 197 (1816)  3) ibid, AnnChim-

**PERCHLORIC ACID**

Überchlorsäure (Ger in the older lit), Perchlorlsäure (Ger), Acide Perchlorique (Fr), Acido Perclorico (It), Ácido Perclórico (Sp), Khalonaya Kislota (Russ); HClO₄, mw 100.46, OB to HCl +64%; mp =102°C (anhyd) (Ref 34) (for mp of hydrates see below); bp 16°C at 18mm with decompn (Ref 17); d 1.7676g/cc at 20°C (Ref 4); RI 1.38189 at 20°C (Ref 19); viss 0.946 centipoise at 20°C (Ref 19); CA Registry No 7601-90-3

**Preparation.** As stated above, perchloric acid was first obtained as a hydrate in 1818, and the anhyd ac was prepd in 1862. At present the anhyd ac is best prepd by vacuum distn of a mixt of 72% ac and fuming sulfuric ac, yield up to 75% (Ref 21). The anhyd ac is unstable, however, and yellows on standing at room temp. The colored ac is extremely sensitive and may expld without warning. Hence anhyd perchloric ac should only be prepd in small ants as needed (Ref 29). Other preps of anhyd perchloric ac are by distn of a mixt of 92% sulfuric ac and K perchlorate (this gives an aq soln of perchloric ac which can be dehydrated as described above) (Ref 10); by passing gaseous HCl thru a satd soln of Na perchlorate, the pptd NaCl filtered off, and the excess HCl driven off during the concn step (Ref 2); and by the action of aqua regia (a mixt of HCl and nitric ac) on AP. Runs on a 500g scale are described, and the process can be readily scaled up (Ref 3). On the coml scale it is prepd by the electrolysis of a soln of chloric ac. Construction details of the electrolysis cell and of its operation are in Ref 38

**Physical Properties.** The IR spectra of solid, liq, and gaseous perchloric ac as well as deuteroperchloric ac are in Ref 33. Its Qf = -11.1 kcal/mole (anhyd) (Ref 20), and -31.6 ± 1.7 kcal/mole (aq soln) (Ref 11)

**Chemical Reactions**

**Water.** The freezing point/compn diagram for w/perchloric ac mixts (Fig 1) shows that at least 6 hydrates are formed (Ref 1, B-2, p 433). The most important of these are:

1) *A Monohydrate*, HClO₄·H₂O, or H₃O⁺ClO₄⁻ as shown by X-ray diffraction (Ref 27) and nuclear magnetic resonance spectral data (Ref 18). It is a hygroscopic solid, mp 49.905 ± 0.005°C (Ref 7), bp 40–50°C at 25mm (Ref 1, B-2, p 436); d₄ 2.040g/cc below -24.9°C, 2.095g/cc above -24.9°C (Ref 26); RI 1.4136 at 50°C (Ref 5); CA Registry No 15979-03-0

It is best prepd by mixing 54.3 parts of 72% perchloric ac with 45.7 parts of 100% perchloric ac. As it is very hygroscopic, it must be sealed in capillaries or otherwise protected from moisture (Ref 27); Qf = -19.7 kcal/mole (Ref 20). It is stable up to 6 months at room temp (Ref 28), and is thermally stable up to 100–10°C (Ref 36) A Dihydrate, HClO₄·2H₂O, or H₃O⁺ClO₄⁻.

H₂O, mp -17.8°C (Ref 22), d₄ 1.7128g/cc at 25°C, RI 1.42052 at 25°C (Ref 8), Qf = -162.8 kcal/mole (Ref 20); CA Registry No 23355-84-4

It is prepd by the addn of 10% by wt of anhyd Mg perchlorate to coml 68–71% perchloric ac, and distn of the mixt at 0.1–1.5mm, yield 40% (Ref 35). It reacts with 99% H peroxide to form a mixed hydrate HClO₄·2H₂O.

H₂O₂, mp = -53°C (Ref 37)

Other hydrates have been prepd which have not been as well characterized as the above (see Fig 1)
Ammonia (see also under ammonium perchlorate). Perchloric ac vapor and anhyd ammonia were reacted in a countercurrent flow reactor with the object of obtaining a stable flame. The vapors were found to react vigorously with the formn of gaseous prods and copious deposits of amm chloride, but a stable flame could not be established (Ref 39)

Antimony and Bismuth. In attempting to dissolve alloys of these metals in hot 72% perchloric ac, a coating was formed which was very sensitive and expl. The chem nature of the deposits was not ascertained (Ref 9)

Metals. It reacts with electropositive metals to evolve H and form metal perchlorates. These reactions must be carried out cautiously as they may proceed with expl violence (Ref 1)

Nitric Acid. Anhyd perchloric ac reacts with 100% nitric ac to form nitronium perchlorate (O₂N⁺ClO₄⁻) (see below) and hydronium perchlorate (see above under hydrates) (Ref 16)

Ozone. Anhyd perchloric ac reacts with ozone when irradiated with light of wavelength 254 m to give HOOCIO₃, which is unstable and decomp to O and chloric ac (Ref 25)

Phosphoric Acid. The two anhyd acids react to form a crys solid which is formulated as (HO)₄P⁺ClO₄⁻ (Ref 19)

Explosive Properties. Aq solns of perchloric ac are insensitive and nonexpl up to their boiling
Mixtures which are Unstable or Explosive

**Dimethyl Sulfoxide.** A violent expn occurs when a drop of 70% perchloric ac is added to 10ml of dimethylsulfoxide (Ref 40).

**Ethanol.** A mixt of 65 parts of perchloric ac, 35 parts of w, & 11.7 parts of et ac has been reported to be a liq expn with a crit diam of 3mm and a deton vel of 100m/sec (Ref 14).

**Hydrogen.** Vapors of perchloric ac form expl mixts with H, hence, in the presence of metals hot perchloric ac can form expl vapor mixts (Ref 12).

**Hydrogen Chloride.** Attempts to prep a complex betw anhyd HCl and anhyd perchloric ac resulted in severe explns (Ref 6).

**Methane.** The vapors of boiling 72% perchloric ac have been found to support the combustion of methane and other organic gases (Ref 39a).

This work has been carried forward in a series of papers in “Combustion and Flame” by G.S. Pearson et al (Vols 8, 199; 11, 97, 103 & 471; 12, 54).

**Sodium Hypophosphite.** One g of Na hypophosphite and 10 drops of 72% perchloric ac expld violently when heated in a procelain crucible (Ref 22).

**Sulfur Trioxide.** An equimolar mixt of S trioxide and perchloric ac, either neat or in chl, forms 2 layers which can deton without warning (Ref 23).

**Trichloroethylene.** Mixts of anhyd perchloric ac with trichloroethylene react with expl violence (Ref 42, p 648).

**Explosive Incidents.** Incidents which have involved mixts with perchloric ac which are normally safe, but which have expld as a result of unusual circumstances or mishandling:

**Acetic Acid and Acetic Anhydride.** Mixts of perchloric ac with these compds are widely used in the metal plating and finishing inds (see below under uses) (Ref 15). Fig 2 shows the triangular phase diagram for perchloric ac/ACO/w (Ref 32), with indications as to those percentages where ign or deton might be expected to occur. One of the most violent ind expls occurred in Los Angeles, Calif on 20 Feb 1947 when an electropolishing bath contg 150gal of 72% perchloric ac and 70gal of ACO detonated. Results: a large mushroom cloud rose over the city (causing rumors of an atomic attack); 17 persons killed, many injured; 116 buildings destroyed, and ca $2 million in damage. Investigation revealed that 1) the cooling coils around the vat had been malfunctioning causing ac to AC to evap, thus enriching the soln in perchloric ac; and 2) a cellulose acetate rack was accidentally introduced into the vat of hot acids, whose oxidn was the immediate cause of the blast (Ref 32).

**Ferrous Sulfate.** A mixt with 72% perchloric ac expld violently on strong and rapid heating. Slow and gentle heating of such mixts is recommended (Ref 42, p 646).

**Methylene Chloride.** On one occasion, in the prep of anhyd perchloric ac in nute chloride, the soln turned yellow and then expld. It was thought that the expln was caused by too rapid mixing of 72% perchloric ac with the P pentoxide dehydrating agent (Ref 41).

**Nitric Acid and Organic Substances.** Mixts of perchloric and nitric ac are frequently used to digest (render w sol) organic materials such as animal and vegetable oils, milk, homogenized animal tissues, etc. If the mixts are heated too rapidly, explns may occur (Ref 42, p 646).

**Thallium Salts.** Although the same prepn had been carried out many times, a violent expln occurred during the evap of a soln of ethylbenzene, TI triacetate, and perchloric ac in acetic ac. No satisfactory explanation for the expln was found (Ref 40).

**Wood.** Over many years the wooden supports of a fume hood had become satu with spillage of chemicals, including perchloric ac and perchlorates. Upon contact with a bunsen burner flame, they expld with great violence (Ref 13).

In summary, ANY mixt of perchloric ac with reducible materials should be regarded as potentially expl and should be handled on the smallest practical scale and behind adequate shielding.

**Uses.**

For reviews see Refs 1 & 30. Its primary use in the expls industry is for the prep of AP and other perchlorates for use in expls, proplnts, and pyrots (see below under individual perchlorates). **As an Electrolyte.** As it is a strong ac and many metal salts are w sol, perchloric ac and solns of perchloric ac in both org and inorg solvs find
many uses in electroplating, electrofinishing, and electropolishing, and electropolishing. Even reactive metals, such as Al and Al alloys, may be cleaned, polished, and plated in perchloric ac solns (Ref 30). In Digestions. Mixts of perchloric and nitric ac are used to digest org materials. For example, in the detn of metals in such materials, they are first refluxed with a mixt of perchloric and nitric ac to oxidize the organic material to C dioxide, oxides of N, and w. The soln is then evapd to dryness and the metal analysis carried out on the residue. An app is described in Ref 24 for carrying out these digestions in a safe manner. The reaction is first carried out under reflux with dilute ac, then when the reaction has subsided, distillate is removed giving a more concd ac which further oxidizes the material. Other Uses. It has also been used as a solv, a catalyst, and as a reagent for the isolation and characterization of org bases by forming insol salts. For details of these uses see Ref 30 and below under perchlorate salts.

Toxicity. Being a strong ac, concd solns are corrosive to the skin and vapors & mists are lung irritants (Refs 31 & 43)

INORGANIC PERCHLORATES

Aluminum Perchlorate [Aluminium Perchlorate (Brit)]. Al(ClO₄)₃, mw 325.37, OB to Al₂O₃ & HCl +29.5%; white delq cryst, mp decomps ca 300° (Ref 7), d 2.209g/cc (Ref 6) (for d of hydrates see below); CA Registry No 14452-39-2

Preparation. The anhyd salt is best prepd by the interaction of anhyd Al chloride and Ag perchlorate in an inert solv thus: Ag perchlorate is heated to reflux in anhyd Me alc in a 3-necked flask protected from w, and anhyd Al chloride in Me alc added dropwise. The pptd Ag chloride is filtered off and the solv stripped at 150° to give an almost quant yield of anhyd Al perchlorate. Benz or toluene may also be used as solvs (Ref 8).

For prep of hydrates see below. The anhyd salt cannot be prepd by removal of w from hydrates as decomp begins before all the w has been driven off (Ref 7)

Properties. It is v sol in w, andaq solns are acidic (reddens litmus paper). Its soly in w is given as 121.6g at 0°, 131.0g at 14.3°, and 148.9g/100ml at 96° (Ref 3). It is also sol in Me & Et alc

Hydrates. Hydrates of Al perchlorate contain 1, 3, 5, 6, 9, 12, & 15 moles of w; but only those contg 3, 6, 9, & 15 moles of w are of any importance:

Al(ClO₄)₃·3H₂O. Mp decomps, d 2.145g/cc. Prepd by heating higher hydrates in vaeuc, and is the lowest hydrate which can be prepd this way (Ref 5)

Al(ClO₄)₃·6H₂O. Delq plates, mp 120.8°, d 2.020g/cc (Ref 5). Weinland & Engraber give the structure as Al(H₂O₆(ClO₄)₃ (Ref 4). It is prepd by dissolving the nonahydrate in boiling 70% perchloric ac and concentrating the soln (Ref 5)

Al(ClO₄)₃·9H₂O. Hygr crysts which require special care in ludling, mp 85.3°, d 1.924g/cc. It is prepd by dissolving Al hydroxide, or better, Al metal, in an excess of 70% perchloric ac on a w bath, cooling the soln to give a gel to which more 70% perchloric ac is added. This breaks the gel and ppts the nonahydrate (Ref 5). DTA shows a strong dehydro endotherm at ca 220° (Ref 9)

Al(ClO₄)₃·15H₂O. Thin, slightly hygr needles, mp 76.2°, d 1.764g/cc. It is prepd by slowly
dissolving an excess of Al hydroxide in 30% perchloric ac on a w bath, cooling the soln to 
-15°, and filtering off the pptd crysts (Ref 5) Other Complexes. Any Al perchlorate hydrate
is placed in a large excess of dimethyl sulfoxide, the solv stripped under the vacuum of a w jet,
the pptd Al(ClO4)3.6Me2SO filtered off, and dried by extn with benz. The product is a useful
expl or expl ingredient (Ref 11)

A series of complexes of the genral formula
MAI(ClO4)4 have been reported either as anhyd
salts or as hydrates. The following have been
prepd:
M = NH4+. Mw 424.87, OB to Al2O3 & HCl
+52.4%. It is prepd by the interaction of AP
and Al perchlorate in liq S dioxide, followed by
evap of the solv. It is recovered as a white
solid, stable up to 50° (Ref 10)
M = Na+. Prepd by Weinland & Engraber (Ref
4) who added Na perchlorate to a soln of Al.
obide in aq perchloric ac; no phys props are
given (Ref 4). More recently workers in the
USSR have reported complexes in which M =
Rb and Cs', which were obtained as dihydrates
by similar procedures (Ref 12). Workers at
Callery Chem Co also prepd a complex in which
M = NO2+, mw 506.78, OB to Al2O3 & HCl
+58.4%. It is prepd by a similar procedure as
that used for the ammonium salt using nitromon
perchlorate, and has similar props (Ref 10)
Uses. (see under Perchlorate Explosives and
Propellants)
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Ammonium Perchlorate [AP, Perchlorate d-
Ammonium (Fr), Ammoniumperchlorat (Ger),
Perchlorato di Ammonio (It), Ammonio Perchlorato
(Sp), Perekhlorata Ammoniya (Russ)]. NH4ClO4,
mw 117.49, OB +27.2%; white rmb crysts
which change to a cubic form at 240° (Ref 15)
and decomp at 265° with evolution of oxides of
N and H chloride (Ref 15) (for further info
on the effects of heat on AP see below); d at
25° 1.9518 = 0.0001g/cc (Ref 7); CA Registry
No 7790-98-9
Preparation. AP was first prepd in 1831 by
Sérullas who neutralized aq perchloric ac with
ammonia and evapd the soln until crysts formed
(Ref 2). The next year it was prepd by Mitscherlich by mixing aq perchloric ac with an aq soln of
diammmonium hexafluorophosphate, the pptd
dipotasium hexafluorophosphate filtered off,
and the filtrate evapd (Ref 3). Later in the 19th
century, AP was prepd by mixing equimolar aq
soins of Ba perchlorate and Amm sulfate, the
solid Ba sulfate filtered off, and the filtrate
evapd (Ref 4). At present AP is best prepd in
the lab by careful neutralization of aq perchloric
ac with gaseous ammonia, the crysts filtered off,
recryst from w, and dried at 110° to const wt
(Ref 6). On the coml scale AP is prepd by the
interaction of Amm chloride and Na perchlorate.
The less-sol AP ppnt and is filtered off, leaving
the NaCl in soln which may be recovered (Ref
19). Flow sheets for the manuf of AP from
ammonia, HCl, and Na perchlorate are given in
Refs 19 & 25. The process described in Ref 19
is continuous and capable of producing ca 5000
lbs/hr. The same process is described in a patent
(Ref 18). In this process anhyd ammonia, 22°Be
aq HCl, 56% aq Na perchlorate, and recycled
mother liquor from the NaCl crystallizer are
metered continuously into a 1000gal glass-lined
reactor heated with steam to 90°. The pH of the
exit stream from this reactor is monitored and
the info fed back to control the addn of HCl
soin to keep the pH of the reaction close to 7.
The exit stream goes to a crystallizer where the
temp is lowered to 35° by vac evaporative cooling, recycled mother liquor added, the mixt passed thru a vaporizer which gives a supersat soln, and then thru a bed of AP cryts where the excess crystallizes. The AP slurry is fed to a centrifuge where the mother liquor is removed and recycled to the AP crystallizer. The AP cryts are washed, dumped into a satd soln of AP which removes last traces of chloride, recenterfuged, and dried in a bldg removed from the mfg operation. The mother liquor and washings from this operation are pumped to the NaCl crystallizer where w is removed in a vacuum evaporator, the pptd NaCl centrifuged off, and the mother liquor recycled to the AP reactor. Fig 1 is a flow sheet of the operation. Economics of the process dictate that a minimum of w be handled thruout the process (Ref 19). Particle size is controlled by rate of crystn or by subsequent processing to produce extremely fine particle AP

_Ultrafine Ammonium Perchlorate (UFAP)._ For high burning rate proplns a fine particle size AP is required and is produced by 3 processes:

a) In a jet mill. Conml AP is fed into a Model 0202 Jet-O-Mizer at a rate of 8 lbs/hr using either N or He at 180°F as the working fluid. The powd prod is collected in trichloroethylene. Best resuts are obtained with He which gave a prod whose particle size was 5μ or smaller (Ref 47)

b) By slurry grinding. A slurry of 85 parts of 1,1,2-trichloro-1,2,2-trifluoroethene (Freon 113), 15 of AP, and 0.15 of XD-7604 surfactant is ground in a Sweco Vibro-Energy mill for 160 hours to give a prod which, when dried, has a particle size of 1.72μ (Ref 48)

c) By freeze-drying. A coned emulsion is made of AP in w plus 1% Nopogen 16-0 emulsifier and 0.1% Johnson’s Wax. The emulsion is freeze-dried in a vac sublimator to give a prod with a residual moisture content of 0.036% and a particle size of 0.37μ (Ref 48). Several variations of this formulation are given in this Ref. Expts were carried out at TCC (Huntsville) to find a coating mat which would prevent cryst regrowth in UFAP. Forty-one compds were examined and best results were obtained with methyl 2-cyanoacrylate (Eastman 910), Johnson’s Paste Wax, and several HX emulsifiers (Ref 48, p 3)

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![Schematic Flow Diagram for the Manufacture of Ammonium Perchlorate](image)

Fig 1  Schematic Flow Diagram for the Manufacture of Ammonium Perchlorate
Ammonium Perchlorate Analysis.

Assay Methods. A Na carbonate fusion prod is currently used for assay of mil grade AP (see below under Specifications), but recently attempts have been made to replace it with a method which is faster and simpler to carry out. Two procs have been proposed:

a) Titanous Chloride Titration. A measured excess of Ti trichloride is added to a known weight of AP which reacts according to the equation:

\[ \text{NH}_4\text{ClO}_4 + 8\text{HCl} + 8\text{TiCl}_3 \rightarrow \]
\[ \text{NH}_4\text{Cl} + 8\text{TiCl}_4 + 4\text{H}_2\text{O} \]

The excess Ti trichloride is then back-titrated with a std ferric amm sulfate soln to a thio-

cyanate end-point. A blank is run concurrently on the Ti trichloride soln. The \% AP in the sample is calc'd by the formula:

\[ \% \text{AP} = \frac{1.4687 \times (B - S)}{W} \]

where:  \( N \) = normality of the ferric amm sulfate soln
\( B \) = vol used in titration of blank
\( S \) = vol used in titration of sample
\( W \) = weight of sample  (Refs 11 & 34)

This proc, while fairly simple and accurate, has the disadvantage that the reagents are unstable, as well as air and moisture sensitive so the titration must be run in a closed system in a CO

dioxide atm. For a diagram of the set-up see Ref 46, p 465

b) Titration in a Nonaqueous Solvent. This proc is based on the enhanced acidity of the Ammon in iso-Pr alc/dimethylformamide, so it can be titrated with a KOH soln according to the equation:

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

using the blue-green end point of thymol blue/phenolphthalein.

Procedure: A 0.05N soln of KOH in iso-Pr alc is prep'd and standardized with primary std benzoic ac. A 0.4g sample is weighed to the nearest 0.1mg into a 250ml erlenmeyer flask. 75ml of a 50/50 mixt by vol of iso-Pr alc & dimethylformamide added, the flask swept with N, 1ml of the indicator soln added, and the soln titrated with KOH soln to a blue-green end point. The \% AP is then calc'd by the equation:

\[ \% \text{AP} = \frac{11.75VN}{W} \]

where:  \( N \) = normality of KOH soln
\( V \) = vol of soln used
\( W \) = weight of sample  (Ref 34, p 17)

This method is quick and fairly easy, but for good results air must be excluded.

Particle Size Analysis. A review of the techniques which have been used to detn the size distribution of fine powds is given in Ref 36: Andreaon Pipette. A sample is dispersed in a liq in a tall column, 10ml samples of the dispersion are withdrawn from a fixed position below the surface at fixed intervals of time, the liq evapd, and the weight of the solids detd. From the height and the fall time, the size distribution can be calc'd using Stoke's Law Coulter Counter. The vol of particles suspended in an electrolyte is detd by the change in resistance as the suspension streams past two closely placed electrodes. The vol is then converted to a particle size distribution

Fisher Sub-Sieve Sizer. Dry air is passed thru a packed bed of the mat and the pressure drop measured. Using curves supplied with the instrument, the surface area is detd and then converted into a particle size distribution

Flying Spot Particle Size Resolver. A moving beam of light scans the sample, the \% light transmitted recorded electronically, and the info fed into the instrument which converts it into a particle size distribution curve

Micrometerograph. The particles are dispersed and injected into the top of a column with compressed N. The wt settling as a function of time is recorded on an automatic balance and converted to a particle size distribution with templates based on Stoke's Law

Mine Safety Appliances Particle Size Analyzer. A dispersion of the sample is placed on top of a liq of greater density. The rate of sedimentation is detd by measuring the sediment vol at fixed time intervals. The results are converted to a size distribution by Stoke's Law

Nitrogen Adsorption. The amt of N adsorbed on a sample is detd by carefully measuring the press change of a known vol of N exposed to a known wt of dry mat at constant temp. The info is used to detn the surface area which is converted to a particle size distribution

Turbidometric Methods. The absorption of a beam of light passing thru a suspended sample in a suitable liq is measured as a function of time.
The info is converted to a size distribution using Stoke's Law.

The most commonly used methods for detn of the particle size distribution of fine AP are the Micromerograph and Turbidometric Methods. For coarser AP samples standard sieves are used (see below under Specifications).

Surface Area Measurements. For a discussion of procs used see above under Fisher Sub-Siever and Nitrogen Adsorption. For AP, the Fisher Sub-Siever is most suitable for samples having surface areas from 0.05 to 0.46 sqcm/g, and the Nitrogen Adsorption method for finer mat, up to 30000 sqcm/cc (Ref 49).

Water Analysis

Nuclear Magnetic Resonance. The sample is dissolved in anhyd (0.02% w) dimethylformamide and the NH₄⁺ peak width at half-height measured at 7.38T and compared with a graph prepd from samples of AP contg known amts of w. The method is accurate up to 7% w (Ref 44).

Karl Fischer Method. See below under Specifications.

Specifications. For mil use, specs have been published for Ammonium Perchlorate (MIL-A-23442A, 8 Sept 1966); Ammonium Perchlorate, Technical (MIL-A-192B, 2 Sept 1965); Ammonium Perchlorate for Solid Propellant Grains Mark 75 & Mark 76 (MIL-A-23946, 19 Aug 1964); and Ammonium Perchlorate, Special, Coarse for Solid Propellant Grains Mark 75 & Mark 76 (MIL-A-23948, 19 Aug 1964). The requirements of the first two specs are:

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<tbody>
<tr>
<td>Assay</td>
<td>99.3%</td>
<td>99.0%</td>
</tr>
<tr>
<td>Total moisture</td>
<td>0.050</td>
<td>0.08</td>
</tr>
<tr>
<td>Surface moisture</td>
<td>0.020</td>
<td>—</td>
</tr>
<tr>
<td>Bromates, as NaBrO₃</td>
<td>0.004</td>
<td>—</td>
</tr>
<tr>
<td>Chloride, as NH₄Cl</td>
<td>0.030</td>
<td>0.15</td>
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<tr>
<td>Chlorates, as NaClO₃</td>
<td>0.020</td>
<td>0.02</td>
</tr>
<tr>
<td>Chromates, as K₂CrO₄</td>
<td>0.015</td>
<td>—</td>
</tr>
<tr>
<td>Iron, as Fe</td>
<td>0.001</td>
<td>—</td>
</tr>
<tr>
<td>Iron, as Fe₂O₃</td>
<td>—</td>
<td>0.0036</td>
</tr>
<tr>
<td>Ash, sulfated</td>
<td>0.300</td>
<td>0.25</td>
</tr>
<tr>
<td>Total water</td>
<td>0.050</td>
<td>—</td>
</tr>
<tr>
<td>Total volatiles</td>
<td>0.040</td>
<td>—</td>
</tr>
<tr>
<td>Particle size</td>
<td>betw 190 &amp; 210μ</td>
<td>—</td>
</tr>
</tbody>
</table>

The last two specs are primarily concerned with particle size. MIL-A-23946 requires 100% to pass thru a 20 mesh sieve and 70% to be retained on a 100 mesh sieve. MIL-A-23948 requires 97% to pass thru a 30 mesh sieve, 35–55% to be retained on a 40 mesh sieve, 90–100% to be retained on a 50 mesh sieve, and 98% to be retained on a 70 mesh sieve.

Ammonium Perchlorate Properties

Briance by Sand Crushing Test. A 0.4g sample, when initiated by 0.25g of Tetryl, crushed 6g of sand (TNT 48g) (Ref 11).

Card Gap Test. Freeze dried UFAP, 0 cards; jet milled UFAP, 0–4 cards; and slurry ground UFAP, 8–10 cards (Ref 48, p 56).

Critical Diameter (which will propagate a detonation). The min diam for dry AP, wet with acet, and wet with et alc, was found to be under 2 inches when confined, and under 4 inches when unconfined (Ref 24).

Critical Height at which a Deflagration-to-Detonation Transition will Occur. Description of test: The mat to be tested is loaded into a 2-inch diameter pipe capped at the lower end. The charge is then ignited at the confined end and any deflagration-to-deton or -expln transition noted. For AP the minimum height for an exphn transition was found to be 12 inches, and over 24 inches for a deton transition (Ref 24).

Detonation Sensitivity. It was found that a No H blasting cap is the min size which will deton AP (Ref 24). Slurry ground and freeze dried UFAP can be detoned by a No 8 blasting cap, but jet milled UFAP failed to deton in 5 tries (Ref 48, p 56).

Detonation Velocity. Dry AP, 3400m/sec; AP wet with et alc, 4200m/sec; and AP wet with acet, 4500m/sec (Ref 24).

Effect of Heat. (see Thermal Decomposition)

Electrostatic Sensitivity. An electrostatic discharge of over 5 joules is required to initiate AP (NG 3 joules) (Ref 24, p 46).

Explosion Temperature. 10sec at 435° (Ref 11).

Flammability. The flammability of AP, as measured by the min weight of a primer which will ignite it, was found to lie betw Xylyl (a Russian expl) and TNT (Ref 38).

Friction Sensitivity. By friction pendulum, it snaps when tested with a steel shoe (Ref 11).

With an ABL-designed sliding friction machine, AP required a sliding dist of 16cm for 50% explns (NC 15cm) (Ref 24, p 20).

Hygroscopicity. When exposed for 192 hours at 21.1 ± 0.1°, AP weight gain was 0.03% at 52%
RH, 0.04% at 75.5% RH, and 0.18% at 90% RH (Ref 12)

**Impact Sensitivity.** With BM app, 91cm for 50% explns, and with PA app, 24 inches for 50% explns, both using a 2kg weight (Ref 11). In Ref 16 the impact sensy of AP is given as 17 inches for 1 expln out of 10 tries with a 2kg weight. By using an “up-and-down” technique, workers at NOL obtained a height of 107cm for 50% explns (Ref 18). The impact sensy of AP doped with various substances was also measured by these workers. Results:

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Height, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP/Amm dichromate, 99/1</td>
<td>95</td>
</tr>
<tr>
<td>AP/Magnetic Fe oxide, 99/1</td>
<td>90</td>
</tr>
<tr>
<td>AP/Mn dioxide, 99/1</td>
<td>88</td>
</tr>
<tr>
<td>AP/sugar/Amm dichromate, 98/1/1</td>
<td>71</td>
</tr>
<tr>
<td>AP/sugar/magnetic Fe oxide, 98/1/1</td>
<td>77</td>
</tr>
<tr>
<td>AP/sugar/Mn dioxide, 98/1/1</td>
<td>65</td>
</tr>
<tr>
<td>AP/sugar/magnetic Fe oxide, 97/1/2</td>
<td>64</td>
</tr>
<tr>
<td>AP/sugar/magnetic Fe oxide, 95/1/4</td>
<td>61</td>
</tr>
<tr>
<td>AP/sugar/magnetic Fe oxide, 93/1/6</td>
<td>84 (Ref 16)</td>
</tr>
</tbody>
</table>

**Heat of Formation.** At 36.6° it is 0.264cal/g/°C (Ref 25, p 552)

**Heat Test.** 75°. All UFAP samples failed to expld after 48 hours at 75° (Ref 48, p 56)

**Heat Test.** 100°. Betw 0 and 48 hours, 1% weight loss; betw 48 and 96 hours, 0.6% weight loss; no explns after 100 hours (Ref 10)

**Ignition and Unconfined Burning Test.** All UFAP samples ignited and burned without expln (Ref 48, p 56)

**Power by Ballistic Mortar.** 100% of TNT (3 tries) (Ref 9)

**Power by Lead Cylinder Compression Test.** 58% of TNT (Ref 8)

**Power by Lead Block Expansion Test.** 46% of PA (Ref 5)

**Solubility.** In w the soly at 0° is 10.92 (d 1.059g/cc), and at 107° (bp of soln) 48.5g in 100g of satd soln (d 1.221g/cc) (Ref 31). In org solv the soly in g/100g of solv are: me alc 6.862, acet 2.260, et alc 1.907, pr alc 0.387, iso-Bu alc 0.127, et acetate 0.032, and bu alc 0.017. It is insol in eth (Ref 6)

**Toxicity.** The toxicity is similar to other perchlorates (see general introduction on Perchlorates)

**Thermal Stability and Effects of Heat.** The thermal stability and thermal decompn of AP have been extensively studied as a starting point for investigations into the decompn and combustn of AP-cont expls and proplnts. Work up to 1968 has been reviewed in Ref 42. In general, the uncatalyzed decompn can be divided into 3 phases: a) A low temp decompn occurring betw 200 and 300° at atm press. The decompn stops before all the AP is consumed. b) A high temp decompn occurring betw 350 and 400°. c) A deflagration or rapid combstn which starts ca 450°. The stoichiometry of the low temp decompn has been concluded to be:

\[
4\text{NH}_4\text{ClO}_4 \rightarrow 2\text{Cl}_2 + 8\text{H}_2\text{O} + 2\text{N}_2 + 3\text{O}_2
\]

(Ref 32)

Small amts of H chloride, N monoxide, N, and other prods which have been found in the decompn of AP are accounted for by secondary reactions and/or higher temp decompns (Ref 42, p 5). Kinetic work on the decompn of AP has been hampered by side reactions and the profound effect which small amts of impurities, especially metal salts, have on the decompn (see below)

At high temps the decompn is believed to be:

\[
2\text{NH}_4\text{ClO}_4 \rightarrow 4\text{H}_2\text{O} + \text{O}_2 + \text{Cl}_2 + 2\text{NO}
\]

(Ref 42, p 8)

More recently the thermal decompn of single large crys of AP has been studied on a hot-stage microscope. It was found that the low temp decompn started on a cryst face as a dark spot which rapidly expanded into a hole which then spread through the cryst. The crysts were not consumed, but a residue of finely powd AP was always left (Ref 45)

**Factors which Catalyze the Decomposition of Ammonium Perchlorate.** Irradiation of AP with X-rays or gamma radiation causes it to decomp at a lower temp, presumably by the formn of “holes” or active sites in the cryst (Ref 36). Metal salts have been found to lower the decompn point of AP by as much as 80° (Ref 39), and to lower the induction period for its expln at 233° by 21 minutes (Ref 41). Inorg salts which have been found to catalyze the decompn of AP are listed below:
<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>22</td>
</tr>
<tr>
<td>CdO</td>
<td>36</td>
</tr>
<tr>
<td>Cd(ClO₄)₂</td>
<td>37</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>30</td>
</tr>
<tr>
<td>Co oxalate</td>
<td>30</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>30</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>29</td>
</tr>
<tr>
<td>Cr₂O₃ + Cr₃O₄</td>
<td>23</td>
</tr>
<tr>
<td>CuCl</td>
<td>29</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>29</td>
</tr>
<tr>
<td>CuCO₃</td>
<td>30</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>30</td>
</tr>
<tr>
<td>Cu Chromite</td>
<td>29</td>
</tr>
<tr>
<td>CuO</td>
<td>29</td>
</tr>
<tr>
<td>Cu(ClO₄)₂</td>
<td>41</td>
</tr>
<tr>
<td>Fe Oxalate</td>
<td>30</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>30</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>28</td>
</tr>
<tr>
<td>Hg(ClO₄)₂</td>
<td>36</td>
</tr>
<tr>
<td>MgO</td>
<td>36</td>
</tr>
<tr>
<td>Mg(ClO₄)₂</td>
<td>37</td>
</tr>
<tr>
<td>MnO</td>
<td>22</td>
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<tr>
<td>HMnO₂</td>
<td>22</td>
</tr>
<tr>
<td>MnCl₃</td>
<td>30</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>22</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>22</td>
</tr>
<tr>
<td>NiCO₃.Ni(OH)₂</td>
<td>30</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>30</td>
</tr>
<tr>
<td>Ni Oxalate</td>
<td>30</td>
</tr>
<tr>
<td>NiO</td>
<td>29</td>
</tr>
<tr>
<td>Ni₂O₃</td>
<td>23</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>30</td>
</tr>
<tr>
<td>ZnO</td>
<td>29</td>
</tr>
<tr>
<td>Zn(ClO₄)₂</td>
<td>37</td>
</tr>
</tbody>
</table>

Uses. (See also under Perchlorate Explosives) Combustible Cartridge Cases. Cotton cloth is impregnated with a slurry of AP and a monomer in methyl ethyl ketone, the solv evapd, and the monomer cured on a mold to give a combustible cartridge case (Ref 35)

Flares. An AP-conig flare is described in Ref 13 which produces little smoke and an intensity of 10000 candlepower

Igniters. A mixt of 3kg of NC, 3.5kg of NG, and 400g of Centralite is homogenized with 100g of dioctyl phthalate, 200g of dye, and 2.98kg of AP (particle size below 60μ), and the mixt pressed into strands 1.5mm in diam which can be used as an ign cord for rocket motors (Ref 43). A Zr/AP mixt (compn unspecified) has the following props: autoign time, 5 sec at 521°F; Qbar 1704 cal/g; threshold ign energy, 1.85cal/sec and d when compressed to 1000psi 2.03g/cc (Ref 40)

Incendiaries. AP has been added to Napalm-type flame agents to raise the flame temp and increase the burning intensity (Ref 17). Graphite, 30 parts; 20 of AP; 13 of polyester; 37 of styrene, 2 of methyl ethyl ketone peroxide, and 0.5 of Co naphthenate are mixed together and cured to give a conductable, flammable plastic with a resistivity of ca 0.7ohm-cm (Ref 21)

Smoke Generating Compositions. A soln of 3 parts of chloronaphthalene in trichloroethylene is slurred with 23 parts of powd Zn and 4 parts of kieselguhr, the solv evapd, the granulated prod mixed with 50 parts of AP and 20 parts of Amm chloride, and the mixt pressed in a mold to give a waterproof smoke generator (Ref 14). A mixt of 50–80 parts of sulfamic ac and 50–20 parts of AP evolves copious amts of smoke on ign (Ref 20). A similar mixt of 390 parts of Zn oxide, 375 parts of hexachloroethane, and 190 parts of AP is slurred in a soln of 40 parts of polyvinyl acetate in 200 parts of mete chloride. The mixt is packed into cylinders, the solv evapd, and ignited to give copious amts of white smoke with a burning time of 68 secs (Ref 26)


**Barium Perchlorate.** \( \text{Ba(ClO}_4\text{)}_2 \), mw 336.27, OB to BaClO +19.0%; colorless hex crystals (called alpha) which change to a cubic form (beta) at 284° (Ref 3) and to a second cubic form (gamma) at 360° (Ref 11), mp 505° with decomp and evolution of O (Ref 14), d 3.681g/cc at 25° (Ref 9); CA Registry No 13465-95-7

**Preparation.** The anhyd salt is prep'd in good yield by heating a mixt of solid Ba chloride and nitrosyl perchlorate (Ref 15), by heating an intimate mixt of AP and Ba carbonate (Ref 8), or by dehydration of the trihydrate in a vacuum at 140–70° (Ref 5)

**Properties.** **Solubilities.** At 25° the soly of Ba
perchlorate in g/100 ml of Me alc is 217.1, Et alc is 124.6, Pr alc is 75.7, isobutyl alc is 56.2, acet is 124.7, and Et acetate is 113.0. It is insol in eth (Ref 4). It is v sol in w: at 0° a satd soln contains 67.3g/100ml of soln, d 1.782g/cc; and at 140° it contains 88.3g/100ml of soln, d 2.230 g/cc (Ref 6)

Other Properties. Heat of Formation. -185.06 ± 0.26 kcal/mole (Ref 18)

Thermal Decomposition. Differential thermal analysis shows phase transitions at 295° and 370° (see above) and a sharp decomp exotherm at 485–500° (Ref 20). G.F. Smith claims that it is unchanged after heating to 400° for long periods of time (Ref 5). Workers in the USSR further investigated the thermal decompn and found that decomp took place betw 320 and 465° with formn of Ba oxide, Ba chloride, and evolution of O. No Ca was evolved below 520–50° (Ref 14)

Hydrates. Ba(ClO₄)₂·2H₂O is prepd by dehydrration of the trihydrate at room temp over P pentoxide (Ref 7)

Ba(ClO₄)₂·2H₂O is pptd when solns of Ba perchlorate are crystd, as in its prep by the action of perchloric ac on Ba carbonate, hydroxide (Ref 2), or chloride (Ref 4); or by the action of a satd soln of AP on Ba hydroxide (Ref 5)

Other Complexes. Complexes are known which contain 1 and 4 moles of ethylenediamine. The complex with 4 moles was found to decomp slowly over a broad temp range, but the one with 1 mole expld shortly after decompn started (Ref 12). A complex is formed with dioxane which is reported to be Ba(ClO₄)₂·2C₄H₈O₂. It forms colorf crystals which lose dioxane on slow heating, but explds violently when heated rapidly to higher temps (Ref 14a)

**Beryllium Perchlorate.** Be(\(\text{ClO}_4\))\(_2\), mw 207.91, OB to BeO and HCl +30.8%; a white hygr powd, mp decomp (Ref 2); CA Registry No 13597-95-0

**Preparation.** It was first prepd by the action of perchloric ac on Be oxide (Ref 2), and more recently by heating a mixt of Be nitrate and excess 70% perchloric ac until fumes appear, cooling, and filtering off the pptd crts (Ref 3)

**Properties.** Its Q\(_f\) was calcd to be -105 kcal/mol (Ref 4). It forms a complex Be(\(\text{ClO}_4\))\(_2\)·4H\(_2\)O.4(dioxane); colorl crts which lose di-oxane on slow heating, expls on rapid heating (Ref 3)

**Refs:** 1) Gmelin, System No 26 (1930), 121
2) C. Marignac, AnnChemPhys 30 (4), 54 (1873)
4) D.E. Wilcox & L.A. Bromley, IEC 55, 32 (1963)

**Cadmium Perchlorate.** Cd(\(\text{ClO}_4\))\(_2\), mw 311.30, OB to CdO & HCl +20.6%; white delq crts, mp 290° with decomp (Ref 2); CA Registry No 13760-37-7

**Preparation.** The anhyd salt can be prepd by the solvolysis of Cd nitrate with anhyd perchloric ac in abs nitric ac (Ref 9); by the action of anhyd perchloric ac on a soln of Cd ions in trifluoroacetic ac (Ref 11); or by the slow dehydration of the hydrates in vacuum (Refs 8 & 15)

**Properties.** Its Q\(_f\) is -49.24 ± 0.42 kcal/mol (Ref 15). Its soly in w at 25° is 4.0 and 50° is 4.8 moles/l (Ref 10)

**Complexes.** Cd(\(\text{ClO}_4\))\(_2\)·2H\(_2\)O. Prepd by the dehydration of the hexahydrate at 90°, then at 130°, at a press of 1mm (Ref 15)

Cd(\(\text{ClO}_4\))\(_2\)·4H\(_2\)O. Prepd by dehydration of the hexahydrate (Ref 2)

Cd(\(\text{ClO}_4\))\(_2\)·6H\(_2\)O. Mp 105°, prep by evapn of Cd oxide (Ref 2) or Cd carbonate (Ref 15) dissolved in excess 70% perchloric ac, recrystd from 79% perchloric ac (Ref 15)

**Cd(\(\text{ClO}_4\))\(_2\)·4NH\(_3\). Prepd by allowing the hexa-ammoniate to stand in air. Effect of heat: begins to lose ammonia at 150°; mp ca 200°; decomp violently above 350°; expls at 400° in a sealed tube (Ref 3)

Cd(\(\text{ClO}_4\))\(_2\)·6NH\(_3\). Prepd by the action of an excess of ammonia on Cd perchlorate (Ref 3). Its expl props are: expln temp 270°; impact sensy (1 kg wt) 53 cm (MF 20 cm); in Trauzl Pb block expansion test, 1 g on deton produced a cavity of 12.6cc (TNT 21.5cc) (Ref 5). It is readily detoned by a No 8 blasting cap contg 0.01g of LA (Ref 4)

**Cd(\(\text{ClO}_4\))\(_2\)·3H\(_2\)O·2.5(dioxane).** Colorl crts, loses dioxane on slow heating, expls on rapid heating (Ref 12)

Cd(\(\text{ClO}_4\))\(_2\)·Cd(OH)\(_2\)·3NH\(_2\)·4H\(_2\)O. Prepd by mixing a soln of 28.6g of Cd perchlorate hexahydrate in 20ml of w with a soln of 50g of hydrazine hydrate in 5ml of w (Ref 6). Its expl props are: expln temp 235°; impact sensy (1 kg wt) 36 cm (MF 20 cm); in the Trauzl Pb block expansion test 1 g on deton produced a cavity of 11.8cc (TNT 21.5cc) (Ref 7)

Use. Cd perchlorate is an efficient catalyst for the decompn and expln of AP (Ref 14). The presence of as little as 0.3% Cd perchlorate in AP lowers its ign temp by 80°, and a 4% mixt will expld at 257° (Ref 13)

**Refs:** 1) Gmelin, System No 33 (1925), 513 & Supp (1959), 92
2) G.G. Sérullas, AnnChimPhys 46 (2), 304 (1831)
3) R. Salvadori, Gazz 42 (II), 458 (1912) & CA 6, 2216 (1912)
4) W. Friederich & P. Vervoorst, SS 21, 67 (1926) & CA 21, 1184 (1927)
5) W. Friederich & P. Vervoorst, SS 21, 95 (1926) & CA 21, 1184 (1927)
6) Ibid, SS 21, 103 (1926) & CA 21, 1184 (1927)
7) Ibid, SS 21, 123 (1926) & CA 21, 1184 (1927)
9) G. Jander & H. Wendt, ZAnorgChem 258, 1 (1949) & CA 43, 6495 (1949)
10) L.S. Lilich & B.F. Dzhurinski, ZhObshChKim 26, 1549 (1956) & CA 51, 4798 (1957)
11) G.S. Fujioka & G.H. Cady, JACS 79, 2451 (1957)
14) F. Solymosi, MagyKemFoly 73, 366 (1967) & CA 68, 6735 (1968)
Calium Perchlorate. Ca(ClO₄)₂, mw 238.98, OB to CaO & HCl +26.8%, colorl, delq crys, mp 220° with decomp (Ref 5); CA Registry No 13477-36-6

Preparation. The anhyd salt is prepd by heating an intimate mixt of one mole of Ca carbonate and 2 moles of AP. Amm carbonate is evolved leaving pure Ca perchlorate (Ref 4). It is also prepd by heating the tetrahydrate to melting at 100°, gradually increasing the temp until all the w is expelled, and finally drying to constant wt at 250° (Ref 3)

Properties. The Qₜ of the anhyd salt was calc'd to be -179 kcal/mole (Ref 8), and of the aq soln to be -173.94 kcal/mole (Ref 6). Effect of heat: Marvin & Woolaver found by thermo-gravimetric analysis that Ca perchlorate starts to decom at 220° and decomp rapidly at 400° to give Ca oxide, Ca chloride, and perchloric ac (Ref 5). Chudinov in the USSR states that it decomp between 320° and 455° with the forms of Ca oxide, Ca chlorde, Cl, and O (Ref 7). Solubility: it is sol in w and most org solv except eth (Ref 3)

Ca(ClO₄)₂.4H₂O. Colorl crys, obtained by evapn of the soln prepd by dissolving Ca oxide or carbonate in aq perchloric ac (Ref 5)

Uses. Incendiary flare compns contg Ca perchlorate are reported in Ref 9


Chromic Perchlorate. Cr(ClO₄)₃, mw 350.30, OB to CrO & HCl +28.5%; only the hexahydrate has been prep as blue-green delq crys, mp 94° (Refs 1, 5 & 6); CA Registry No 13537-21-8

Preparation. By dissolving hydrated chromic oxide in 20% perchloric ac followed by evapn of the soln (Ref 4)

Effect of Heat. In 1910, R. Roth reported that the blue-green hexahydrate turns green on heating. At 110° w is lost, then perchloric ac, followed by decomp at 210° into chromyl chloride and chromic ac (Ref 3)

It forms a complex with 6 moles of dimethyl sulfoxide which is stable to 195°, but expls betw 200 and 235° (Ref 8)

Chromyl Perchlorate. CrO₂(ClO₄)₂, mw 282.89, OB to CrO & HCl +25.5%; a red liq, bp 36° under high vac (Ref 2 & 7). It darkens on cooling to dry ice temp and is stable for about a

Cesium Perchlorate. CsClO₄, mw 232.26, OB to Cs₂O & HCl +13.8%; rhombic crys which change to a cubic form at 219°; mp 250° with decomp; d 3.327g/cc (Ref 7). Gordon & Campbell say that they found by differential thermal analysis that the phase transition point is 224°, the mp is 575°, and that decomp occurs at 628−30° (Ref 2); CA Registry No 13454-84-7
month at this temp. It decomp at room temp, explosively in the presence of light; and flames in the presence of org mat. (Ref 7)

Refs: 1) Gmelin, System No 52, Part B (1962), 260
2) Ibid, 279
3) R. Roth, "Zur Kenntnis der Perchlorate", München, (1910), thru Mellor, 1st Ed 2 (1922), 403
4) R.F. Weinland & F. Ensgraber, ZAnorgChem 84, 368 (1913) & CA 8, 878 (1914)
5) V. Biber et al, JGenChemUSSR 7, 2658 (1937) & CA 32, 2044 (1938)
6) I. Neiman, JGenChemUSSR 10, 723 (1940) & CA 35, 24334 (1941)

Cobalt Perchlorate (Cobaltous Perchlorate), Co(ClO₄)₂, mw 257.83, OB to CoO and HCl +24.8%; red needles, d 3.327g/cc (Ref 28); CA Registry No 13455-31-7

Preparation. The anhyd salt can be prepd by treating the hexahydrate with a large excess of 2,2-dimethoxypropane; and the excess reagent, acet., and Me alc distd off to give two liq phases. The lower phase solidifies to a complex of Co perchlorate with Me alc which can be desolvated by careful heating (Ref 27). Caution: prepn of anhyd perchlorates by this procedure has been reported to result in violent expls if the mixts are heated above 65°C (Ref 26). An etherate is obtained by the reaction of anhyd Co bromide with Ag perchlorate in eth (Ref 16)

Complexes

Hydrates. Co(ClO₄)₂·4H₂O. A violet solid, prepd by dehydration of the hexahydrate at 180°C. It decomps rapidly above 180°C with the evolution of O, Cl, and H chloride (Ref 4)

Co(ClO₄)₂·6H₂O. Long red hexagonal prisms, mp above 100°C with decomp (Ref 4). It is prepd by dissolving Co carbonate or oxide in aq perchloric ac followed by evap of the soln (Ref 10). It detons on percussion and deflgr on rapid heating (Ref 3)

Co(NH₄)_2(ClO₄)₂. Violet crys., prepd by heating the hexa-ammoniate to 80°C. It decomps at 170°C, rapidly at 220°C, and expls at ca 256°C (Ref 21)

Co(NH₄)₃(ClO₄)₂. Light brown cubic crys. (Refs 9 & 24), prepd by dehydration of the hexahydrate with 2,2-dimethoxypropane followed by the addn of anhyd ammonia to the soln (Ref 24), or by the addn of aq ammonia to a soln of Co perchlorate in O-free w contg an excess of perchloric ac (Ref 9). Expln temp: 275°C; impact sensy with 1 kg wt, 55cm for 50% expls (MF 20cm); power by Trauzl Pb block expansion test: 1 g, upon deton, made a cavity of 18.6cc (TNT 21.5cc) (Ref 6)

Co(N₂H₄)₂(ClO₄)₂. Expln temp 215°C; impact sensy for 50% expls with 1 kg wt, 20cm (MF 20cm) (Ref 7)

Uses. At a level of 1%, anhyd Co perchlorate was found to increase the burning rate of a propellant formulation from 0.07 to 0.12 inches/sec at 1000ps (Ref 20)

Cobaltic Perchlorate. Co(ClO₄)₃. It is known only in the form of complex salts (see below)

Co(NH₄)₂(ClO₄)₃. It has been reported to have a high impact sensy and to expld at 320°C (Ref 29)

Co(NH₄)₃(ClO₄)₃. Yellow cubic crys. (Refs 9 & 12); prepd by the action of perchloric ac on Co hexammino trinitrate in abs nitric ac (Ref 12). Qf = 307kcal/mole (Ref 2); expln temp 360°C; impact sensy with 2kg wt, 18cm for 50% expls (LA 10cm); power by sand test: 1 g, when initiated with 0.25g of MF, crushed 39.2g of sand (TNT 42.0g) (Ref 11)

CoCl(NH₃)₂(ClO₄)₂. Carmine red lustrous crys. powd (Ref 17); prepd by soln of Co aquo-penta-ammino perchlorate in N-hydrochloric ac, evap of the soln, and recrystn of the solid obtained from dil perchloric ac (Ref 17); or, by treatment of Co chloropenta-ammino dichloride with concd perchloric ac, the soln cooled in ice, the crys. filt'd, and dried (Ref 25). Qf = 252.8 kcal/mole (Ref 18, p 428); expln temp 320°C; impact sensy with 2kg wt for 50% expls, 21cm (LA 10cm); power by sand test: 1 g, when initiated with 0.25g of MF, crushed 30.6g of sand (TNT 42.0g) (Ref 11)

CoPH₃(NH₃)₂(ClO₄)₂. A sample of the dry mat was reported to have expld when touched with a hot Pt wire (Ref 29, p 673)

CoSCN(NH₃)₂(ClO₄)₂. Deep rose red needles; prepd by the addn of aq Na perchlorate to an ice cold soln of Co thiocyanato penta-ammino dithiocyanates, the pink solid filtered, and dried (Ref 19); by the addn of aq Na perchlorate to the sulfate (Ref 15); or by the addn of Na thiocyante to Co aquo-penta-ammino diperoxylolate
(Ref 23). Expln temp 375°C; impact sensy with 2kg wt, 55cm for 50% explns (LA 10cm); power by sand test: 1 g, when initiated with 0.2g of MF, crushed 20.1g of sand (TNT 42.0g) (Ref 11).

Co₂(NH₃)₄ClO₄. Deep red cubic crystals (Ref 8); prepd by the action of perchloric ac on Co aquoammonio-ammonio dichloride (Ref 5). Impact sensy with 2kg wt, 21cm for 50% explns. The expln is described as strong with a visible flame and loud report (Ref 25).

CoCl₂(NH₃)₄ClO₄. Impact sensy with 2kg wt, 20cm for 50% explns (RDX 25cm) (Ref 25)

Co(NO₃)₂(NH₃)₄ClO₄. Brownish yellow crystals; prepd by the action of perchloric ac on Co dinitro-tetra-ammonio nitrate in w (Ref 5). Impact sensy with 2kg wt for 50% explns, cis-isomer, 36cm; trans-isomer, 59cm (AP 22cm). The expln is described as strong with a visible flame and loud report (Ref 18).

Co(SCN)₂(NH₃)₄ClO₄. Expln temp 335°C; impact sensy with 2kg wt, 35cm for 50% explns (LA 10cm); power by sand test: 1 g, when initiated with 0.2g of MF, crushed 13.9g of sand (TNT 42.0g) (Ref 11).

Co(H₂O)₂(NH₃)₄ClO₄. Brownish red octahedral crystals (Ref 13); prepd by the action of aq perchloric ac on Co carbonato tetra-ammonio nitrate (Ref 22). Impact sensy with 2kg wt for 50% explns, 24cm. The expln is described as strong with a visible flame and loud report (Ref 25).


**Copper Perchlorate (Cupric Perchlorate).**

Cu(ClO₄)₂, mw 262.43, OB to CuO and HCl +24.4%; green monoclinic crystals, mp 82.3°C (Ref 21), bp subl under high vac (Ref 13), d at 23°C 2.255g/cc (Ref 21), Qf —19kcal/mole (Ref 9); CA Registry No 13770-18-8

**Preparation.** The anhyd salt is prepd by heating in vac at 200°C a mixt of nitrosyl perchlorate (NOClO₄) and either Cu monoxide, dichloride, nitrate, or perchlorate dihydrate. Lower temps favor the formm of mixts of Cu nitrate and perchlorate. The last traces of nitrate can be removed by fractional subln (Ref 13). It is also prepd by the action of nitrosyl perchlorate on powd Cu in org solvs (Ref 14)

**Complexes**

**Hydrates.** Cu(ClO₄)₂·2H₂O. Prepd by the action of perchloric ac on Cu carbonate followed by evapn of the soln (Ref 6); d at 20°C, 1.955g/cc (Ref 3)

**Cu(ClO₄)₂·6H₂O.** Light blue delq triclinic crystals, mp 82°C (Ref 21). It is prepd by dis-
solving Cu monoxide in aq perchloric ac followed by evapn of the soln (Ref 2), or by allowing the heptahydrate to stand over P pentoxide (Ref 6). It soly in w is 54.3g/100ml of soln (Ref 6), and it is sol in et alc and eth (Ref 21). It is also very sol in dimethylformamide and its UV and Visible spectra have been measured in this solv (Ref 10). Its thermal decomp by differential thermal analysis has been studied and shows that the dehydration occurs in two steps at 93 and 282° followed immediately by a strong exotherm at 300–400° (Ref 11)

\textbf{Cu(NH₃)₄ClO₃} \textsubscript{2}. Blue-violet to violet crysts (Ref 7); d at 25°, 1.952g/cc (Ref 6). It is prepd by dehydration of the hexahydrate in an excess of 2,2-dimethoxypropane followed by addn of anhyd ammonia to the soln (Ref 16)

\textbf{Explosive Properties}

\textbf{Burning Rate.} Samples were compressed into Plexiglas tubes 7mm in diam and the burning rate vs press measured. At 1 atm it was found to be ca 1g/secm-sec and at 100 atm 27g/secm-sec (Refs 19 & 20)

\textbf{Explosion Temperature.} 260° (Ref 4), 269.5° (Ref 8)

\textbf{Impact Sensitivity.} 50cm for 50% expls with 1 kg wt (MF 20cm) (Ref 4)

\textbf{Power by Trauzl Lead Block Expansion Test.} 1 g, when initiataed by a No 8 blasting cap, formed a cavity of 14.2cc (TNT 21.5cc) (Ref 4)

\textbf{Sensitivity to Initiation.} It is readily initiataed by 0.01g of LA (Ref 4)

\textbf{Cu(N₂H₄)₂ClO₄} \textsubscript{2}. A sens solid, expln temp ca 35° (Ref 5)

\textbf{Uses:} Addn of 1 mole % of anhyd Cu perchlorate lowers the decomp point of K perchlorate from 618 to 525° (Ref 15). Addn of 0.015 mole % to AP lowers the induction period for its decomp at 233° from 27±4 to 6±2 mins (Ref 17). Cu perchlorate has been patented as a burning rate modifier in solid proptns (Ref 12)


\textbf{Fluorammonium Perchlorate (Fluorammonium Perchlorate).} FN₃H₃ClO₄, mw 135.48, OB +35.4%; white hygr solid, mp 104–5, with decomp; sol in esters, nitrites, nitroalkanes, and tetrahydrofuran, insol in hydrocarbons and halocarbons; impact sensy similar to RDX. Prep’d by the hydrolysis of et or iso-Pr N-fluorocarbamate in a soln of anhyd perchloric ac in chlf

\textit{Refs:} 1) Gmelin, not found 2) V. Graukauskas et al, JACS 90, 3839 (1968)

\textbf{Fluorine Perchlorate.} (Supplements article in Vol 6, F135-R). From hydrolysis data the Qf was calcld to be +37.6 ± 9 kcal/mole (Ref 2); CA Registry No 10049-03-3


\textbf{Hydrazine Perchlorate.} (See in Vol 7, H200-R); CA Registry No 13762-80-6
Hydrazine Diperchlorate (Hydrazinium Diperchlorate; in Gmelin it is called Hydrazonium Dypyroperchlorate, HDP). \( \text{N}_2\text{H}_4\cdot 2\text{HClO}_4 \), mw 232.97, OB +34.3%; white crusts, mp 191\(^\circ\), d 2.21g/cc (Ref 4); CA Registry No 13812-39-0

**Preparation.** HDP was first prepd by the interaction of equimolar amts of \( \text{aq} \) Ba perchlorate and hydrazine sulfate, the pptd Ba sulfate filtered off, and the filtrate evaporated in a w bath until crust occurs (Ref 2). It has also been prepd by the interaction of 2 moles of \( \text{aq} \) perchloric acid and 1 mole of hydrazine hydrate followed by evapn of the w or its azetotropic removal by distn with trichloroethylene (Ref 6), or by sweeping hydrazine vapors into 70% perchloric acid with dry N (Ref 7)

**Properties**

**Heat of Formation:** \(-70 \pm 1 \text{kcal/mole}\) (Ref 3)

**Impact Sensitivity.** Explds with a hammer blow (Ref 2)

**Thermal Stability.** Impure prepns turn yellow on standing at RT (Ref 2). When heated it shows a slow press increase starting at 120\(^\circ\) due to evolution of 1 mole of perchloric acid followed by an extremely sharp press rise due to the decomp of the monoperchlorate (Ref 5)

**Uses.** It has been proposed as a high energy proplnt ingredient, but high cost and hygroscopicity have precluded general acceptance (Ref 4)


Iron Perchlorate (Ferrous Perchlorate). \( \text{Fe(ClO}_4\text{)}_2 \), mw 254.75, OB to FeO and HCl +25.1%. It is only known in the form of hydrates, the most well known being the hexahydrate, \( \text{Fe(ClO}_4\text{)}_2\cdot 6\text{H}_2\text{O} \); long green crystals, stable in air (Ref 2), \( Q_F \) calc’d to be \(-56\text{kcal/mole}\) (Ref 5); CA Registry No 13933-23-8

**Preparation.** It is prepd by the action of 70% perchloric acid on Fe sulfide (Ref 2), or sulfate (Ref 7) followed by evapn of the soln. **Caution:** strong heating of the mixt of perchloric acid and Fe sulfate was reported to result in a violent expln; gentle heating is recommended (Ref 7). An etherate was prepd by the interaction of Ag perchlorate and Ag dibromide in eth (Ref 3)

**Uses.** The addn of 0.03 to 0.29 mole % of the hexahydrate lowers the decomp point of AP to 100\(^\circ\) (Ref 6). It has been patented as a burning rate accelerator in solid propnts (Ref 4)


Lead Perchlorate. \( \text{Pb(ClO}_4\text{)}_2 \), mw 406.09, OB to PbO & HCl +15.8%. The anhyd salt is a white solid which is extremely hygroscopic and can only be handled in the dry atm of a glove box (Ref 3), mp 270–5\(^\circ\) with decomp (Ref 3); \( d_d \) at 25\(^\circ\), 4.84g/cc (Ref 1); CA Registry No 13637-76-8

**Preparation.** The anhyd salt is prepd by drying the trihydrate over P pentoxide in a vacuum at 65\(^\circ\) for 19 hours, then at 100\(^\circ\) for 10 hours, and finally at 120\(^\circ\) for 14 hours (Ref 3). More recently workers in the USSR have reported a similar proc in which the hydrate is dried at 2–4mm as the temp is raised slowly from 10 to 200–20\(^\circ\) (Ref 4)

**Effect of Heat.** Anhyd Pb perchlorate is stable up to 200\(^\circ\), begins to decomp at ca 250\(^\circ\) with the evolution of Cl and O, and decomps completely above 275\(^\circ\) (Ref 3). The Russian workers

Hydroxylamine Perchlorate (Hydroxylaminium Perchlorate, HAP). (See Vol 7, H245-R); CA Registry No 15588-62-2
found that the decompn prods are Pb monoxide, Pb dichloride, Cl, and O (Ref 4)

\[ Pb(ClO_4)_2 \cdot 3H_2O \]. White rhombic crysts (Ref 6), mp 83–4\(^\circ\)C (Ref 3); bp, decomp ca 100\(^\circ\)C, d 2.6

g/cc (Ref 6). It is prepd by dissolving Pb carbonate in aq perchloric ac followed by evapn of the
soln until crystals appear (Ref 2), or by allowing the anhyd salt to stand in a moist atm (Ref 3).
It is very sol in w and alc 20 (Ref 6). An almost satd soln in m alc was reported to have expld violently upon manipulation. Care in handling such solns is recommended (Ref 3)


Magnesium Perchlorate. Mg(ClO_4)_2, mw 223.21.

OB to MgO & HCl 112.78%; white delq crystals, melts with decompn over a wide temp range
betw 244 & 520\(^\circ\)C (Ref 10); d at 18\(^\circ\)C 2.21g/cc (Ref 15); Qf \(-140.6\) kcal/mole (Ref 9); CA Registry No 10034-81-8

Preparation. The anhyd salt is best prepd by drying the hydrate first in a stream of dry air at 170\(^\circ\)C, then in a vacuum over P pentoxide at 250\(^\circ\)C to remove the last traces of w (Ref 2).
It may also be prepd by heating an intimate mixt of AP and Mg carbonate at 200\(^\circ\)C and
1–10mm (Ref 5)

Effect of Heat. The anhyd salt was found to decomp betw 320 & 450\(^\circ\)C.
The decomp is autocatalyzed by the O evolved, and the prods are Mg oxide, Mg chloride, O and Cl (Ref 12).
The addn of 1.75 mole % to AP raises its decomp rate at 273\(^\circ\)C from 1.8 to 5.9 \times 10^4 g/min; and a 20 mole % mixt decompss at 7.9 \times 10^2 g/min (Ref 13)

Hydrates. The only important hydrate is the hexahydrate, Mg(H_2O)_6(ClO_4)_2, long rhombic needles, mp 185–90\(^\circ\)C (Ref 15), d at 25\(^\circ\)C, 1.970

g/cc (Ref 4); prepd by dissolving pure Mg oxide in dil perchloric ac, evapor the soln until fumes appear, and cooling. The solid crystals are filtered out and recrystd from w (Ref 2)

Impact Sensitivity. On the ERL machine the anhyd salt had a 50% expln height of 254cm

sandpaper and over 320cm without sandpaper. A mixt with 2% sugar had 50% expln heights of 135cm and over 320cm respectively (Ref 11)

Lithium Perchlorate (updates article in Vol 7, L45). OB to Li_2O and HCl \(60.0\%\); CA Registry No 7791-03-9

Preparation. The anhyd salt is prepd by dehydrating at 300\(^\circ\)C of the trihydrate, which is prepd
by evapn of solns prepd by the interaction of Li sulfate and Ba perchlorate (Ref 4), or by the
action of aq perchloric ac on an excess of Li carbonate (Ref 2). Both the anhyd salt and the
trihydrate are coml compds, and their manuf has been reviewed (Ref 5). Workers in the USSR have prepd it by the electrolysis of aq Li perchlorate using Pt electrodes (Ref 3)

Uses. Addn refs to the use of Li perchlorate in oxygen producing compns (oxyrn gas cylinders) are in Refs 6 & 7. These compns have been proposed as substitutes for compressed or liq oxygen in enclosed spaces such as spacecraft cabins and submarines (Ref 6). A mixt of 35g of amon Si and 65g of Li perchlorate was compressed into a cylinder at 2000psi and ignited with an ignitacord fuse to give a dense white smoke whose obscuring power was 5000cu ft/lb (Ref 8); a similar mixt of 6 parts of powd B and
4 parts of Li perchlorate also is a smoke generating compn (Ref 9).

Refs: 1) Gmelin, System No 20 (1927), 166, Supp (1960), 404 2) G. Scatchard et al,
Solubilities. The anhyd salt is very sol in w, me alc, et alc, pr alc, Bu alc, ac et, and et acetate; but only sl sol in eth (Ref 3)

Uses. Anhyd Mg perchlorate has found widespread use as a drying agent under the trade names Anhydron and Dehydrinit. This use has been reviewed in a book by G.F. Smith (Ref 6).

It has an advantage over many other drying agents as it can be readily regenerated by dehydration at 250–300° (Ref 12). It is especially useful in packing drying towers for drying gases. Extreme care must be taken, however, in drying org comds as exlns can result. For example, contact of anhyd Mg perchlorate with a hydrocarbon gas contaminated with Bu fluoride caused a purple discoloration of the solid, followed almost immediately by an exln (Ref 7). Upon attempted regeneration of a sample of Mg perchlorate which had been used to dry olefins, it exptd when the temp reached 220° (Ref 8).

On another occasion, upon addn of tri-methyl phosphate to anhyd Mg perchlorate, the mixt exptd with injury to the operator (Ref 12a).

Anhyd Mg perchlorate was added to a mixt of Bu acrylate and acrylonitrile, and the mixt polymerized in a 2.75 inch mold to give an illuminating flare of 2 million CP (Ref 14).


Manganese Perchlorate (Manganese Perchlorate).

Mn(ClO₄)₂, m w 253.84, OB to MnO & HCl +25.2%; the hexahydrate is obtained as pale rose needles (Ref 2); Qₜ calc’d to be ~90kcal/mole (Ref 5); CA Registry No 13770-16-6

Preparation. The hexahydrate, Mn(H₂O)₆(ClO₄)₂, has been prep’d by dissolving Mn hydroxide or carbonate in diox perchloric ac followed by evapn of the soln until crystals appear (Ref 2). Attempts to dehydrate it by heating with an excess of 2,2-dimethoxypropane resulted in severe exlns when the temp was raised above 65° (Ref 6).

Effect of Heat. The hexahydrate loses 2 moles of w at 115° to form a tetrahydrate which decomps with formn of Mn dioxide at 145–50°. Around 195° it expts (Ref 3).

Uses. A Mn perchlorate (degree of hydration unspecified) has been patented as a burning rate accelerator for solid propjets (Ref 4).


Mercury Perchlorate (Mercuric Perchlorate).

Hg(ClO₄)₂, mw 399.49, OB to HgO & HCl +16.0%; white microcryst solid (Ref 2); Qₜ –17kcal/mole (Ref 4); CA Registry No 7616-83-3

Preparation. The anhyd salt is prep’d by the addn of a soln of perchloric ac in trifluoroacetic ac to that of a Hg salt in the same solv, followed by careful evapn of the solv until crystals form (Ref 2).

Uses. It has been reported to be an efficient
catalyst for the decomp and expln of AP (Ref 3)


Nickel Perchlorate (Nickelous Perchlorate).

Ni(ClO₄)₂, mw 257.61, OB to NiO & HCl +24.8%; a yellow solid, d 3.4g/cc (Ref 20); CA Registry No 13637-71-3

Preparation. The anhyd salt is prep'd by treating the hexahydrate with a large excess of 2,2-dimethoxypropane. Two phases are obtained with most of the Ni perchlorate in the lower phase. After several hours a solid sep's from this phase which is filtered off and dried to give Ni perchlorate contg ca 0.5% w (Ref 20).

Caution: On one occasion, in the use of this proc, a violent expln occurred when the mixt was heated above 65° (Ref 18). It has also been prepd by dissolving Ni oxide or carbonate in anhyd trifluoroacetic ac followed by addn of anhyd perchloric ac. The pptd solid is filtered off and dried in a vacuum to remove trifluoroacetic ac (Ref 12)

Complexes. Hydrates with 9, 7, 6, 5, 4, & 2 moles of w are known, but only the hexahydrate, Ni(H₂O)₆(ClO₄)₂ is of any importance. It is obtained as long green hexagonal needles, mp 209° (Ref 8), by the action of Ni sulfate on Ba perchlorate; or by dissolving Ni hydroxide (Ref 14), nitrate, or carbonate (Ref 13) in dl perchloric ac followed by evap of the soln, filtering, and drying the crystals formed. It is very sol in dimethylformamide, and its visible spectrum has been measured in this solv (Ref 10)

Ni(NH₄)₂(ClO₄)₂. Lavender crystals, prep'd as follows: to a soln of 23.8g of Ni dichloride and 5.4g of Amm chloride in 125ml of w is added 14.0g of Na perchlorate in 50ml of w, followed by the slow addn with stirring of 60ml of concd aq ammonia. The mixt is chilled for 4 hours in an ice bath and the solid filtered to give 48% of the hexammoniate which is free of chloride (Ref 11). It also can be prep'd by treatment of an O-free aq soln of Ni perchlorate contg an excess of perchloric ac with aq ammonia, filtering off the crystals, and drying (Ref 15); or by the dehydration of Ni perchlorate hexahydrate with an excess of 2,2-dimethoxypropane and adding anhyd ammonia to this soln (Ref 16). The compd is very insol in w and can be used for the quant detn of Ni (Ref 9)

Explosive Properties.

Burning Rate. 1.90g/sqcm/sec at 60atm. The rate is almost independent of press betw 1 and 100atm (Ref 19)

Detonation Sensitivity. It is readily detoned by a No 8 blasting cap contg 0.01g of LA (Ref 3)

Detonation Velocity. 5303m/sec (Ref 4)

Explosion Temperature. 275° (Ref 3)

Heat of Combustion. 260kcal/mole (Ref 19)

Impact Sensitivity. With a 1 kg wt., 55cm for 50% explns (MF 20cm) (Ref 3); with a 2kg wt., 9 inches for 50% explns (Ref 11)

Power by Trauzl Lead Block Expansion Test.

A l g sample, on deton, formed a cavity of 19.7cc (TNT 21.5cc) (Ref 3)

Thermal Decomposition. Betw 80 & 140° a reversible deamination occurs with the loss of 4 moles of ammonia, and betw 240 & 280° an irreversible exothermic reaction occurs resulting in an expln at ca 280°. A residue of Ni oxide contg some chloride is left (Ref 17)

Hydrazine Complex. A complex with the empirical compn Ni(ClO₄)₂Ni(OH)ClO₄,5N₂H₄.H₂O has been reported to be a pale blue solid (Ref 5) with the following expl props:

Effectiveness as a Detonator. Wts of the subs which will initiate the following expls are:

- Tetryl 0.10g, TNT 0.15g, & TNAnS 0.45g (Ref 7)

Explosion Temperature. 175° (Ref 6)

Impact Sensitivity. With a 1 kg wt., 19cm for 50% explns (MF 20cm) (Ref 6)

Power by Trauzl Lead Block Expansion Test. A l g sample formed a cavity of 19.5cc on deton (TNT 21.5cc) (Ref 6)

Nitrosyl Perchlorate. NOClO₄, mw 120.46, OB +36.5%; white hygr orthorhombic cists (Ref 3), d 2.162g/cc (Ref 4); CA Registry No 15605-28-4

Preparation. It was first prepd by passing a mixt of N monoxide and N dioxide into 72% perchloric ac, the mixt evap until the temp rose to 140° and dense white fumes were evolved, and cooled. The solid which sepd was found to be a monohydrate of nitrosyl perchlorate which was dried in a vacuum over P pentoxide to give the anhyd salt (Ref 2). More recently it was obtained by the action of an excess of liq dinitrogen tetroxide on anhyd Mg perchlorate (Ref 5)

Properties
Reactions. It reacts with w to form N oxides, with me alc to form NMe₄, and expls on contact with dry eth or amines (Ref 2)

Thermal Decomposition. Workers at the Hebrew Univ, Israel found that the thermal decomp of nitrosyl perchlorate at 100–140° results in an equilibrium being established with nitryl perchlorate and the decomp prods of both compds (nitronium). N dioxide, Cl dioxide, and O were found to be the final decomp prods isolated (Ref 6)

Refs: 1) Gmelin, System No 6, Part B-2 (1969), 533
2) K.H. Hofmann & G.A. Zedwitz, Ber 42, 2031 (1909)
3) L.J. Klinkenberg, Rec 56, 749 (1937) & CA 31, 7307 (1937)
4) K. Cruse et al, ZAnorgChem 259, 154 (1949) & CA 44, 5251 (1950)

Nitryl Perchlorate (Nitroxy I Perchlorate, Nitronium Perchlorate). NO₂ClO₄, mw 161.45, OB +29.7%; colorless monoclinic hygr cryst; mp decomp above 135° without exp; CA Registry No 17495-81-7

Structure. Earlier workers considered it to be the mixed anhydride of nitric and perchloric acids (O₂NOClO₄) (Ref 3), but later, as a result of X-ray (Ref 5) and Raman spectroscopic work (Ref 8), it was shown to be an ionic salt with distinct NO₂⁺ and ClO₄⁻ ions present in the cryst lattice

Preparation. It was first prepd in an impure form by Hantzsch who isolated a cryst solid when anhyd nitric and perchloric acids were mixed. He reported the solid to be ON(OH)₂⁺ClO₄⁻ (Ref 2), but later work by Goddard and co-workers showed this solid to be a mixt of nitronium perchlorate and perchloric ac monohydrate (Ref 4). It is best prepd by distilling anhyd perchloric ac onto an excess of dry dinitrogen pentoxide at −80°, the mixt allowed to warm to room temp, and the mixt pumped under vacuum for 2 days to remove volatiles. The residue was shown by analysis to be a mixt of 89 mole % nitronium perchlorate and 11 mole % perchloric ac hydrate. Pure nitronium perchlorate was obtained by repeating the exp for NMe₄ and using a large excess of dinitrogen pentoxide (Ref 6)

Properties. It is very sol in nitric ac and may be recrystd from this solv (Ref 7). It is a strong oxidizing and nitrating agent, and flames or expls on contact with org compds. In soln in NMe₄ it is less reactive and can be used in this solv as a nitrating agent. Benz, for example, is instantly nitrated to NB on contact with a NMe₄ soln of nitronium perchlorate, but further nitrination takes place very slowly (Ref 7)

Uses. Attempts have been made to use nitronium perchlorate as a high energy propellant ingredient, but incompatibility with other ingredients and hygroscopicity have combined to hinder such use (Ref 9)

Refs: 1) Gmelin, System No 6, Part B-2 (1969), 536
2) A. Hantzsch, Ber 58B, 941 (1925)
3) W.E. Gordon & J.W.T. Spinks, CanJRes B 18, 358 (1940) & CA 35, 1336 (1941)
4) D.R. Goddard et al, Nature 158, 480 (1946)
5) E.G. Cox et al, Nature 162, 259 (1948)
6) D.R. Goddard et al, JCS 1950, 2550

**Potassium Perchlorate.** KClO₄, mw 138.55, OB to K₂O & HCl -46.2%; white rhomb crys solid which is transformed to a cubic form at 300° and melts at 588° with decomp (Ref 16); d at 0°, 2.53574 + 0.0001g/cc (Ref 11); Qf -111.29kcal/mole (Ref 14); CA Registry No 7778-74-7

**Preparation.** The early history of the prepn of K perchlorate by the action of acids on K chloride is reviewed in Ref 3. These authors found that treatment of 2-5g of K chloride with 50ml of concd sulfuric acid gave an 11% yield of K perchlorate. The sulfuric acid must be added slowly with cooling to the K chloride, or explns may result. Similarly, nitric acid gave a yield of 15-30%, 85% phosphoric acid gave a yield of 15%, and Cr trioxide gave a yield of 12-15%. Org acids failed to yield any perchlorate when heated with K chloride (Ref 3). It can also be prepd by heating a mixt of solid K chloride with nitrosyl perchlorate (ONClO₄). Nitrosyl chloride is evolved and a residue of K perchlorate is left (Ref 26). On a corin scale, K perchlorate is prepd by mixing hot aq solns of Na perchlorate and K chloride. Upon cooling, Na chloride is pptd and filtered off. Upon further cooling, the K perchlorate seps and is recrystd from hot w (Ref 18). The manuf has been reviewed (Ref 21). Prior to 1958 prodn was betw 784 and 4370 tons/yr at a cost of 18.5-20 cents/lb (Ref 19, p 87)

**Impact Sensitivity.** K perchlorate and mixts of it with 1% ferric oxide, Mn dioxide, sugar, Amm dichromate, and a 50/50 mixt with Amm nitrate were all insensitive to impact (over 320cm) with a 2.5kg wt (Ref 13)

**Solubility.** In w at 0° it is 0.75; at 100°, 18.2; and at 265°, 70g/100ml of satd soln. These values are smoothed data from several earlier sources (Ref 27, p 178). Solys in org solvs are given in Ref 27, p 187

**Effect of Heat.** The thermal decompn is said to be sharp at 510° to give K chloride and O (Ref 7). Bircumshaw & Phillips, however, state that the decompn is complicated and irreproducible in a vacuum, with Cl as well as O and K chloride being formed (Ref 8)

**Explosion Temperature.** The expln temp of 80/20 mixts of K perchlorate with org compds was found to be: ethylene glycol, 240°; polyester resin, 290°; and cotton linters, 245°. The addn of 1% K chloride, Li chloride, or Li bromide failed to change these temps (Ref 15)

**Uses** (see also under Perchlorate Propellants and Explosives):

**Delay Compositions** (comps used in fuses and other timing devices and which have an exactly predetermined burning rate). A mixt of 54.5% Ba chromate, 30.5% powd W, 10% K perchlorate, and 5% Si dioxide has a Qf of 38sec/sec, and burning rates of 29.7sec/inch at 15psi and 18.7 sec/inch at 1200psi (Ref 4). Similar mixts of 45.5-49.5% Ba chromate, 35-9% powd W, 10% K perchlorate, 5% diatomaceous earth, and 1.0-1.5% Ba or Zn stearate have burning rates of 11.8768-12.8962sec/inch at -65°F, and 12.5313-13.1420sec/inch at 71°F (Ref 34). Compns of 54% Zr/Ni alloy, 31% Ba chromate, and 15% K perchlorate have burning rates which can be varied by using alloys of 70/30, 50/50, or 30/70 Zr/Ni. The burning rates are ca 1:2:3 respectively (Ref 22, p 283). Spec for ml W delays are in MIL-T-23132 (1961). A similar series of fuse powder contg mixts of Zr/Ni and Ti/Ni alloys, Ba chromate, and K perchlorate are described in Ref 31. The burning rates can be varied betw 2 and 25sec/inch by changing the compn

**Flares, Signaling Devices, and other Pyrotechnics.** A large number of formulations contg K perchlorate have been reported. Some devices which use these are: red RK signal flares (Refs 2 & 22, p 275); parachute flares (Ref 6); "stars" for use in signaling pistols (Very pistols) (Refs 5 & 22, p 275); variously colored flares (Refs 19; pp 197-8 & 22, p 275); "stars" and other components of display fireworkes (Refs 16 & 32);
and "whistlers" (Ref 22, p 280)

**Combustible Cartridge Cases.** Cotton gauze is impregnated with a mix of 70% K perchlorate, 14.5% et cellulose, 9.6% Neolyn 23 curing agent, and 6.2% plasticizer; the impregnated cloth is formed into cartridge cases, and cured to give, combustible cartridge cases (Ref 29)

**Igniters.** A pellet composed of 26.5% K perchlorate, 16.6% Ba nitrates, 53.9% 50/50 Zr/Ni alloy, and 3.0% et cellulose can be used to ignite solid proplnt grains (Ref 25). A series of mixes of K perchlorate with powd metals and other oxidizable mat were examined as substitutes for BPA/Pd as a gun primer. Most of the mixes tested were found to be satisfactory and to be compatible with brass and other metals (Ref 9)

**Incendiary Compositions.** Stoichiometric mixes of K perchlorate with metals and oxidizable mat have been proposed as incendiaries of the Thermit type and have heats of reaction as follows: Al dust 2504, powd Mg 2429, red P 1477, powd S 705 and powd C (lampblack) 1118cal/g (Ref 4). A mix of 12.5% K perchlorate, 75% powd Zr, and 12.5% of a 50/50 Al/Mg alloy is reported to be a readily-ignited incendiary (Ref 20). Mixt of powd Al and/or powd Fe with K perchlorate with 1.5–2% NC as a binder are also good incendiaries (Ref 35)

A mix of 35% Ca silicide, 35% powd Sb, 30% K perchlorate, and 5% NC is listed as a fire starter mixt (Ref 22, p 282). A mixt of 40 parts of powd Al, 60 parts of K perchlorate, and 4 parts of chlorinated rubber were placed in a hole drilled in concrete and ignited, resulting in the concrete being shattered without any expln (Ref 33)

**Photoflash Compositions.** Workers at PicArsn have investigated a series of mixes of K perchlorate with powd metals for use as photoflash compns. Info on candlepower, time to peak luminosity, and duration of flash, as well as performance at sea level and 1 x 10^5 feet, are given for each compn (Ref 23). A standard mil photoflash compn is given as 40% atomized Al, 30% Ba nitrates, and 30% K perchlorate (Ref 22, p 274)

**Smoke Generating Compositions.** A series of mixes of K perchlorate with powd Zn, hexachloroethane, and/or C black is reported in Ref 12. Temp stability info is also included in this Ref. A compn of 42.7% K perchlorate, 22.3% powd Al, 18.1% hexachloroethane, and 16.9% Li carbonate forms a dense smoke on ignition which is hygroscopic, giving a denser smoke cloud in moist air (Ref 28). Another somewhat different compn of 50–80 parts of sulfamic ac and 20–50 parts of K perchlorate is claimed to produce dense smoke on combustion (Ref 17)

**Tracers.** To a mixt of 34 parts of Laminac resin, 4 of benzyl alc, 2 of Co naphthenate, and 4 of me et ketone peroxide is added an equal wt of a mixt of 1 part of powd Mg and 2 of K perchlorate. The mixt is formed and cured to give a tracer for following visibly the path of rockets (Ref 24). In Ref 16, p 275 are given formulations for mixt contg K perchlorate which is used in tracer ammo for automatic small arms. Tracer compns contg powd Zr which are suitable for modern HV small arms are discussed in Ref 30

**Specification.** The requirements for mil grade material are covered in Mil Spec MIL-P-217A, Amendment 1 (1966). Two grades are listed, Grade A and Grade B; their chemical requirements are detailed in Table 1

### Table 1

<table>
<thead>
<tr>
<th>Potassium Perchlorate—Chemical Requirements</th>
<th>Percent by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grade A</td>
</tr>
<tr>
<td>Moisture, max</td>
<td>0.02</td>
</tr>
<tr>
<td>Chlorides (as KCl), max</td>
<td>0.10</td>
</tr>
<tr>
<td>Chlorates (as KClO₃), max</td>
<td>0.10</td>
</tr>
<tr>
<td>Hypochlorites</td>
<td>None</td>
</tr>
<tr>
<td>Bromates (as KBrO₃), max</td>
<td>0.02</td>
</tr>
<tr>
<td>Sodium (as NaClO₃), max</td>
<td>0.20</td>
</tr>
<tr>
<td>Calcium and Magnesium salts (as oxides), max</td>
<td>0.20</td>
</tr>
<tr>
<td>Grit and Water insoluble material, max</td>
<td>0.02</td>
</tr>
<tr>
<td>Iron (as Fe₂O₃), max</td>
<td>–</td>
</tr>
<tr>
<td>pH of water solution</td>
<td>7.0 ± 1.5</td>
</tr>
<tr>
<td>Assay KClO₄, min</td>
<td>99.0</td>
</tr>
</tbody>
</table>

Five classes of KClO₄ are given based on particle size. These are: Class I – 99.9% by wt passing US Standard Sieve No 40 (420 micron); Class 2 – 99.9% by wt passing US Standard Sieve No 100 (149 micron); Class 3 – 99% by wt min passing US Standard Sieve No 80 (177
micron), and 80–90% by wt passing US Standard Sieve No 200 (74 micron); Class 4 – Average particle diameter 20 ± 5 microns by Fisher Sub-Sieve Sizer; Class 5 – Average particle diameter 70 ± 30 microns by Fisher Sub-Sieve Sizer.

**Refs:**
1. Gmelin, System No 22 (1936), 502
2. L.S. Ross, USP 1094259 (1914) & CA 8, 2227 (1914)
3. V. Lenher et al, JACS 44, 143 (1922)
4. A. Stettbacher, Protar 10, 158 (1944) & CA 39, 2203 (1945)
5. L.H. Erickson & O.E. Sheffield, “Substitutes for Potassium Perchlorate in Pyrotechnic Compositions”, PATR 1408 (1944), AD 496017
15. J. Grodzinski, JApplChem 8, 523 (1958)
16. R.G. Hall, USP 2841481 (1958) & CA 52, 17716 (1958)
17. S.J. Magrums, USP 2842502 (1958) & CA 52, 17717 (1958)
23. S. Lopatin, Sea-Level and High-Altitude Performance of Experimental Photoflash Compositions”, PA FRL-TR-29 (1961), AD 266213
26. M.M. Markowitz & P.R. Winterntz, USP 3110558 (1963) & CA 60, 6519 (1964)

**Addnl Refs** (limited distribution):

**Rubidium Perchlorate.** RbClO_4, mw 184.92, OB to Rb_2O and HCl +34.6%; white rhomb crystals which change to a cubic form at 281° and melt at 606° with decompos (Ref 2); d at 25°, 2.80 g/cc; RI at 25°, 1.4701 (Ref 6); CA Registry No 13510-42-4

**Preparation.** It is prepd by dissolving Rb carbonate in dil aq perchloric ac, evap the soln until crystals appear, filtering, and drying the crystals at 120° (Ref 3). Workers in the USSR have reported its large scale prodn by a similar process (Ref 5)

**Effect of Heat.** Differential thermal analysis shows an exotherm above the mp at 625–35°
Silver Perchlorate. AgClO₄, mw 207.32, OB to Ag₂O and HCl +30.9%; white delq rhomb crystals, mp 486°F with decomp; d at 25°C, 2.806g/cc (Ref 15); Qₚ = 7.44 kcal/mole (Ref 13); CA Registry No 7783-93-9.

Preparation. It was first prep by dissolving Ag oxide in aq perchloric acid followed by evapn of the soln until crystals form (Ref 3). More recent procedures for the prep of the anhyd salt are by the addn of anhyd perchloric acid to the soln of a Ag salt in trifluoroacetic acid (Ref 9); by the interaction of solid nitrosyl perchlorate and Ag bromide (Ref 10); or by the addn of the monohydrate to et bz. Two phases are formed, the upper phase contg only et bz and Ag perchlorate. This phase is treated with a satd hydrocarbon to gve anhyd Ag perchlorate (Ref 13). Last traces of w can be removed by azeotropic distn with bz (Ref 11).

Solubilities. A remarkable prop of Ag perchlorate is its extremely high solv in w and org solvs. For example, 557g will dissolve in 100ml of w at 25°C, d of the soln 2.8478g/cc (Ref 4). Some solvs in org solvs are: aniline 5.3, pyridine 26.4, toluene 101 (Ref 5), and eth 19.2g/100ml (Ref 7). It is also sol in glycerol, acetic ac, nitro methane, nitrobenzene, and chlorobenzene; but insol in chlf and C tetrachloride (Ref 5).

Explosion Temperature. 800°F (Ref 2).

Impact Sensitivity. After recryst from eth, a sample expld violently on crushing in a mortar. It was assumed that either an etherate or occluding eth caused the expln (Ref 8). A similar incident occurred, however, where there was no evidence of the presence of org subs (Ref 16).

Uses. Ag perchlorate has been patented as a burning rate accelerator for solid propants (Ref 6). Solid Ag perchlorate has been used as a catalyst for the ign of hydrazine as a monopropellant (Ref 12).

Sodium Perchlorate. NaClO₄, mw 122.44, OB to Na₂O & HCl +52.3%; white rhomb crystals which change to the cubic form at 313°C, melt at 473°C, and decomp at 480°C (Ref 8) into NaCl and O (Ref 7); d 2.5298g/cc (Ref 10); Qₚ = 91.48 ± 0.22 kcal/mole (Ref 12); CA Registry No 7601-89-0.

The anhyd salt is obtained when samples are recrystd from w above 53°C; below this temp a monohydrate is obtained (see below). The pure salt is best obtained on a lab scale by dissolving pure Na carbonate in a slight excess of dil aq perchloric acid, the soln partly evapd, cooled to 50°C, the solid centrifuged off, and dried in a current of air at 250°C. Similar results were obtained starting with pure Na chloride (Ref 2). On a com scale it is prepd by the electrolysis of Na chloride (see Vol 2, C197-R). Processing details and economics of the prep are given in Refs 5 & 11. Concld solns are used, and modern plants use continuous electrolytic cells. In 1960 prod was estimated to be ca 10000 tons/year at a cost of 17.56$/lb (Ref 11, p 87).

Hydrates. Monohydrate, NaClO₄·H₂O, hygr crystals, mp 130°C with loss of w. It is obtained.
when concd aq solns are recrystd below 50° (Ref 1). A sesquihydrate, 2NaClO₄·H₂O, and a trihydrate have also been reported (Ref 1)

**Impact Sensitivity.** Pure Na perchlorate and mixts with 1–2% of various subjs were found to be insensitive to impact (over 320cm) (Ref 9)

**Solubilities.** In g/100g of solv the solys are: w 209.6, me alc 51.4, acet 51.7, et alc 14.7, pr alc 4.89, bu alc 1.86, et acetate 9.65 and iso-Bu alc 0.786. It is insol in eth (Ref 3)

**Toxicity.** Injection of aq Na perchlorate into rabbits caused no long term toxic effects. It behaved as a mild muscular poison, and large doses caused liver damage and diarrhea. Goldfish will live indefinitely in a 0.1% soln, but a 1% soln will cause asphyxia (Ref 4)

**Uses.** The primary use for Na perchlorate is in the mgf of other perchlorates and most of the prodn is used captively by the same plant which made it (Ref 11, p 87). Other uses which have been reported follow:

**Flares.** A flare comp is described in Refs 15 & 16 contg powd Mg, Na perchlorate, and a binder which can be cast and cured, and which has a luminous intensity of 50,500 candle-sec/g

**Incendiaries.** A mixt of 100g of Na perchlorate and 58.7g of powd Al has a Q₇ of 2751cal/g and can be used as a filler for incendiary bombs (Ref 6). A proc is described in Ref 14 for coating Na perchlorate with Al, and the use of the coated material in incendiaries

**Photoflash Compositions.** Mixts of 80% Ca metal and 20% Na perchlorate; and 80% Ca, 10% Na perchlorate, and 10% Na nitrate have been examined as expt photoflash compts for both sea level and high altitude use (Ref 13)


**Strontium Perchlorate.** Sr(ClO₄)₂, mw 286.52, OB to SrO & HCl +22.3%; white delq rhomb crysts; decomp vigorously at 477° (Ref 6); d₄ at 25°, 2.973g/cc (Ref 5); Q₉ (calcd) −187 kcal/mole (Ref 9); CA Registry No 13450-97-0

**Preparation.** It is prepd by dissolving pure Sr nitrate in an excess of perchloric ac, the excess ac neutralized with Sr carbonate, all solids centrifuged off, and the soln chilled until crysts appear (Ref 2). The anhyd salt can also be prepd by drying the hydrate at 250°, yield 50% (Ref 3); or the addn of anhyd perchloric ac to a soln of Sr ion in anhyd trifluoroacetic ac, the pptd solid filtered, and the excess ac removed in a vacuum (Ref 7)

**Solubilities.** Soly in g/100g of solv are: w 309.7, me alc 221.0, et alc 180.7, pr alc 140.4, bu alc 113.5, iso-Bu alc 77.9, acet 140.1, and et acetate 136.9. It is insol in eth (Ref 2)

**Uses.** (see also under Perchlorate Propellants and Explosives). It is used in pyrotechnics to impart a bright red color to flames (Ref 3). A gel was made from 50g of Sr perchlorate, 100g of me alc, and 4.6g of Carbopol 940 gelling agent. Five g of this gel burned for 10 mins with an intense red flame (Ref 11). A 66/34 mixt of Sr perchlorate/powd Al was tested as a photoflash comp for both sea level and high altitude use (Ref 8). Another mixt of 50ml of me
methacrylate. 165g of Sr perchlorate, and 3 drops of cumene hydroperoxide was polymerized in a mold to give a candle which burned for 30 secs with a bright red flame 24 inches high (Ref 10)


Titanium Perchlorates

Titanyl Perchlorate. OTi(ClO₄)₂, mw 262.80, OB to TiO₂ & HCl +27.4%; colorless hex tablets contg an undetd number of moles of w (Ref 1). Later work indicates that the compd is probably a mixt of penta and tetra hydrates (Ref 10)

Preparation. By dissolving 1 mole of anhyd Ti tetrachloride in 2 moles of anhyd perchloric ac, and the viscous yellow soln evapd in a vacuum at 30-40° to give colorl crystals (Refs 1 & 2)

- It forms an expl compd with dioxane

Titanium Tetrachloride. Ti(ClO₄)₄, mw 445.70, OB to TiO₂ & HCl +30.5%; CA Registry No 13498-15-2

Preparation. Anhyd perchloric ac and Ti tetrachloride were combined in a mol ratio of 8:1 at -10° to give a cryst solid whose purity by analysis was 97-8% (Ref 3)

Properties. It can be stored at low temps in the absence of air or w, and is described as a powerful oxidant which is insensitive to shock, but expls on contact with eth, and flames on contact with formamide or dimethyl formamide (Ref 3)

An excess of dinitrogen tetroxide is condensed onto Ti tetrachloride at liq N temp and the excess removed by vacuum distn to give a complex Ti(ClO₄)₂·N₂O₄ (Ref 4), which is described as very hygr and as being a useful dessicant, nitrating agent, and oxidizing agent (Ref 5)


Uranyl Perchlorate. UO₂(ClO₄)₂, mw 469.0, OB to UO₂ & HCl +15.4%. The hexahydrate is obtained as monoclinic crystls, mp 90° (Ref 1), CA Registry No 13093-00-0

Preparation. U tetroxide is dissolved in 40% aq perchloric ac, the soln concd on a w bath, and chilled to give yellow crystls of the hexahydrate (Ref 3). Attempted recrystn of this salt from et alc resulted in an expln (Ref 2)


Zinc Perchlorate (Zink Perchlorat (Ger))

Zn(ClO₄)₂, mw 264.27, OB to ZnO & HCl +24.2%; Q₆ = -37.42kcal/mole (Ref 11), CA Registry No 13637-61-1

Preparation. The anhyd salt has only recently been prepd by heating a mixt of Zn oxide and nitrosyl perchlorate in a vacuum at ca 180° (Ref 11)

Complexes. Hexahydrate. Zn(ClO₄)₂·6H₂O, white thumb crystls, mp 106°, decomp at 200°, d 2.252 ± 0.01g/cc (Ref 12). It was first prepd by interacting aq solns of Zn sulfate and Ba perchlorate, filtering off the pptd Ba sulfate, and evapng the soln until crystls appear (Ref 2). It has also been prepd by dissolving Zn oxide or carbonate in aq perchloric ac and evapng the soln until crystls appear (Ref 4). The hexahydrate loses 2 moles of w at its mp to form a tetrahydrte which on further heating decomp at 260° (Ref 4)
Solubilities of Hexahydrate. In w at 20°, the
solv is 32.4 moles/l (Ref 8); in cellosolve, 130 g
is sol in 100cc of soln; and in furfural, 100g will
dissolve in 100cc of soln (Ref 7). It is also sol-
in et aici (Ref 4)

Tetra-ammoniate. Zn(ClO₄)₂.4NH₃, small tetra-
headrals crys, mp 220°, decomp rapidly at
250°, explds on rapid heating (Ref 3). It is
prepd by the addn of an aq soln of AP to
the soln of a Zn salt in aq ammonia (Ref 3); or by
the dehydration of the hexahydrate with a large
excess of 2,2-dimethoxypropane, followed by
the addn of anhyd ammonia to the soln. The ppt
is filtered off and dried (Ref 9)

Explosive Properties of Tetra-ammoniate.

Explosion Temperature. 305° (Ref 5)

Impact Sensitivity. With a 1 kg wt, 70cm for
50% explns (MF 20cm) (Ref 5)

Power by Trauss Lead Block Expansion Test.
1 g, on ign, formed a vol of 15.1cc (TNT 21.5cc)
(Ref 5)

A hydrazinate has been prepd which could
not be analyzed because of extreme sensy
(Ref 6)

Uses. Anhyd Zn perchlorate is a good catalyst
for the decompn and exphn of AP (Ref 10)

Refs: 1) Gmelin, System No 32, Supp (1956),
883 2) G.S. Sérimas, AnnChimPhys(2) 46,
304 (1831) 3) R. Salvadori, Gazz 40 11,
19 (1910) & CA 5, 1717 (1911) 4) R. Salva-
dori, Gazz 42 1, 458 (1912) & CA 6, 2216
(1912) 5) W. Frederich & P. Vervoort, SS
21, 65 (1926) & CA 21, 1184 (1927) 6) W.
Frederich & P. Vervoort, SS 21, 103 (1926)
& CA 21, 1184 (1927) 7) A.L. Chaney &
C.A. Mann, JPhyChem 35, 2289 (1931) & CA
25, 5099 (1931) 8) K. Schwabe, ZElectro-
Chem 39, 791 (1933) & CA 28, 47 (1934)
9) B.B. Wayland & W.L. Rice, InorgChem 6,
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73, 366 (1967) & CA 68, 6731 (1968) 11)
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12) ChemRubHdb (1975–6), B-158

Inorganic Perchlorate Explosives. Expls contg
one of the inorganic perchlorates (primarily K or
Amm perchlorate) or perchloric acid as one of
the principal ingredients

Alfred Nobel first proposed using inorganic
perchlorates in expls, and in 1885 patented
some proplnts contg thm. They were not
successful. However, when used in blasting expls
(in lieu of chlorates), it was found that they were
very suitable ingredients. With the introduction
of electrolytic methods of manuf of the per-
chlorates in the 1890’s, the extensive use of these
compds in both commercial and military expls
was inaugurated. Sweden and Switzerland were
the first to use blasting expls contg perchlorates
extensively

Certain advantages of perchlorates over Dyna-
mite or other NG expls for a number of specific
applications were soon recognized. One of the
outstanding features of perchlorate expls is their
greater safety due to being much less sensitive
to shock, particularly at lower temps where
freezing seriously affects the safe handling of
NG expls. Also, in warm climates, perchlorates
are free from exudation tendencies, and they
are relatively nontoxic compared with Dynamite.
In general, their expl action is slower than that
of NG, but they are capable of producing a rela-
tively greater expl effect. Their adaptability
covers quite a wide range. For example, by
using mixts of K and Amm perchlorate in varying
ratio, by adding Na nitrate, or by incorporating
other types of expl materials such as nitro-
organic compds, the expl action may be adjusted
to suit the particular material to be blasted.
Either hard or soft rock can be shattered into
small pieces, or only broken into large blocks as
in the case of the quarrying of building stone.
Dynamite, on the other hand, exerts a more
nearly constant effect which tends toward the
shattering side. The action of perchlorate
expls seems to extend laterally more than in the
case of Dynamite, which is more local in its
action (Ref 17)

Following is a listing of past and present
inorganic perchlorate expls which are detailed
 thruout the Encyclopedia:

Ajax Powder, Alcalsits (Alkalsits), Alvisi
Explosive; Berges, Corbin et Cie Explosifs A,
B, I, II and III; Blastine, Burrows Explosive,
Carbonites, Cheddites (Perchlorate), Cremonita,
Dynobel, Explosif P, Frazer Explosive (for
clearing mine fields), Gesteinspermonit, Gesteins-
persalit, Herculite, Kainpites, Kratits, Lheure
Explosives, Manilante, M.B. Powder, Neomals,
Nisser Powder, O'Brien Explosive, Ophorite,

Although perchorlates are still more expensive than chlorates, their use can be justified by the following advantages: 1) perchlorates contain more available oxygen per unit weight than the corresponding chlorates, and are more stable; 2) they are less sensitive to mechanical action, and for this reason it is not necessary that each particle be encapsulated in resilient material to diminish the sensitivity, as is the case with chlorate expls; and 3) as an additional advantage, Amm perchlorate produces only gaseous products, but these unfortunately include the toxic hydrogen chloride. These gases are not objectionable when expls are used in bombs, mortar shells or in open pit mining; but are objectionable when used in confined spaces. However, they can be rendered harmless if nitrates (10 to 20%) are incorporated, as was done in some German Perchlorits, Swedish Territ, English Blastine and Belgian Yonckite. The incorporation of MnO₂ (up to 18%) also acts as an inhibitor of HCl formation.

Although perchlorate expls are fairly insensitive to mechanical action, they are, nevertheless, too sensitive for some applications. Incorporation of materials such as paraffin (as was done in the French Perammon and the English Blastine) or of castor oil (as was done in some Swiss expls), renders them quite plastic and insensitive to shock and friction. This addition might make these expls too insensitive to an initiating agent. In order to counteract this defect, small quantities of NG (as low as 4%) may be incorporated, as was done in some Perchloratits. The addition of NG not only makes the mixt more readily detonatable but it also helps to plasticize the expl, especially if aromatic nitrocompds, such as DNT, TNT, etc, are also present.

When perchlorate expls are used in gaseous mines, a cooling agent must be incorporated. For example, Wetterperchlorit and Yonckite 10 bis, have Na chloride incorporated; some Perchlorits, Permonits, Telsits, etc, contain AN; and Ajax Powder, Herculite, Neonals, etc, have Amm oxalate as a cooling agent.

It should be noted that the incorporation of substances such as TNT increased the sensitivity to initiation, and the addition of AN increased the quantity of expln gases, while at the same time diminishing the sensitivity of the perchlorate expl to open flame.

Refs: See below under Inorganic Perchlorate Military Explosives.

Inorganic Perchlorate Military Explosives. Due to the shortage of aromatic nitrocompds such as TNT, several European countries, during WWI and even during WWII, used expls contg K or Amm perchlorate.

According to Stettbacher (Ref 11, Vol 1), the Germans during WWI used a mixt (called “Deutscher geschlossbarer Minensprengstoff”) consisting of K perchlorate 56, DNB 32 and DNN 12%, which was cast-loaded in trench mortar shells, land mines and various bombs, while the French used “Perammon” (qv) for loading aerial bombs.

Marshall (Ref 1, Vol 3) states that the British used a mild but hot expl, “Ophorite” (qv), during WWI as an opening charge for incendiary shells and smoke bombs.

According to Davis (Ref 12), during WWII the Germans used an expl called “Perdit” (qv) in their trench mortar shells. Its compn was identical to that given by Stettbacher for “Deutscher geschlossbarer Minensprengstoff” above. Davis also relates that the French used a mixt consisting of Amm perchlorate 86 and paraffin 14% for loading their 75mm shells.

Both Davis (Ref 12) and Nasium (Ref 8) affirm that the following compn was used by the French during WWI for loading 58mm trench mortar shells; Amm perchlorate 74.5, paraffin 17, and Al powder 8.5%.

According to Stettbacher (Ref 11, Vol 2), an expl contg Amm perchlorate 90 and paraffin 10%, was used for military purposes under the name “Perammon” (qv). This seems to be the same expl as “Perammon”, used by the French during WWI.

A rather unusual application for a military perchlorate expl is covered by a US patent issued to Frazer et al (Ref 16) on producing
surface explns over large areas. This is intended primarily as a means of clearing fields of land mines. The area is first sprayed with a mixt of concd perchloric acid and a miscible organic liq of low volatility, such as ethylene glycol monooethyl ether. The sprayed film is then detonated by suitable means, such as a grenade, in order to expel the mines in the area.


Perchlorit (Perchlorites). A type of Ger perchlorate mining expl used prior to and during WWI. Two typical formulations are shown in Table 1:

Table 1

<table>
<thead>
<tr>
<th>Ingredients and properties</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>K perchlorate</td>
<td>35</td>
</tr>
<tr>
<td>Amm nitrate</td>
<td>42</td>
</tr>
<tr>
<td>DNT*</td>
<td>10</td>
</tr>
<tr>
<td>DNN</td>
<td>4</td>
</tr>
<tr>
<td>Wood meal</td>
<td>5</td>
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<tr>
<td>Coal powder</td>
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<tr>
<td>Oxygen Balance, %</td>
<td>+1.7</td>
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<tr>
<td>Trauz Test, cc</td>
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</tbody>
</table>

*DNT was prepd by the nitration of m-MNT

Refs: 1) Naoum, NG (1928), 133 2) PATR 2510 (1958), Ger 129-R

Perchlorocellulose, Perchloronitrocellulose, Perchloroglycerin and Perchloronitroglycerin. A series of expls prepd by Alvisi (BelgP 141582 of 1899) by treating cellulose or glycercin with either perchloric acid alone, or with mixts of perchloric and nitric acids

Ref: Daniel (1902), 606

Perchormic and Perpolypercormic Acids and Their Salts

Monoperchormic or Permonochromic Acid, HCrO₃, or Monoperchormates, MeCrO₃ or R.CrO₃, where Me stands for a metal and R for an organic radical. The acid has not been isolated, but some of its salts were prepd by O. Wiede in 1897 (Ref 3). Its K salt can be obtained by treating a cold sulfuric acid soln of K₂Cr₂O₇ with an excess of H₂O₂. It is a violet, unstable product to which the structural formula (KO.O)CrO₃ was assigned. Wiede, Riesenberg
and others prepared the following organic salts and additive compounds of monoperchloric acid: Tetramethylammonium Monoperchlorate, $\text{NH}_4\text{ClO}_7$. Violet prisms; can be kept in the cold for several days; dissolves in $w$ with a brown coloration.

Pyridine Monoperchlorate. $\text{CsH}_2\text{N.HClO}_4$. Blue, rhombic plates, fairly stable when dry. It detonates when heated, or on contact with concd sulfuric acid.

Diperchomeric Acid. $\text{H}_3\text{CrO}_7$ or $(\text{HO.O})_2\text{CrO}_2\cdot(\text{OH})$ and Diperchomates, $\text{R.H}_2\text{CrO}_7$, also called "Blue Perchlorates". The compounds were discovered by Wiede (Ref 3), and were also obtained by Hofmann et al (Ref 4) and Riesenfeld et al (Ref 5). The latter investigators prepared the blue perchlorates by the action of 30% hydrogen peroxide on an acidic solution of a chromate Ammonium Diperchomate. $(\text{NH}_4)\text{H}_2\text{CrO}_7$. Bluish-black or violet crystals. When dry, it can be kept for several days at RT, dissolves in ice cold $w$, forming a violet-brown liq which gives a neutral reaction. When heated rapidly the salt burns with a hissing noise.

Potassium Diperchomate. $\text{K.H}_2\text{CrO}_7$. Exists in the form of red and dark violet modifications. The dark violet powder detonates at slightly above 0°.

In general, all diperchomates are less stable than triperchomates, which are described below.

Triperchomeric or Hypermonoperchloric Acid, $\text{H}_3\text{CrO}_8$ or $(\text{HO.O})_2\text{CrO}_2$ and Triperchomates, $\text{R}_3\text{CrO}_8$, also called "Red Perchlorates", were first prepared by Riesenfeld et al (Refs 1, 5 & 6). The alkaline salts can be obtained by treating an alkaline solution of chromic acid with 30% hydrogen peroxide. The K salts can be obtained by slowly adding a K dichromate soln in concd sulfuric acid to q$w$ hydrogen peroxide Ammonium Triperchomate. $(\text{NH}_4)\text{H}_2\text{CrO}_8$ or $(\text{NH}_4\text{O.O})_2\text{CrO}_2$. Reddish-brown octahedral crystals; explodes when heated to about 50° or above. Si sol in $w$; insol in alc and eth. It decomps rapidly at 40°. When dry it can be kept for several days without decomposing. Potassium Triperchomate. $\text{K}_3\text{CrO}_8$. Dark red

prisms which can be kept for a month when dry without decomposing. Si sol in $w$; insol in alc and eth. It decamps explosively at about 178°, or when in contact with concd sulfuric acid. The impure salt is more expl.

Sodium Triperchomate. $\text{Na}_3\text{CrO}_8$. Reddish-yellow plates which cannot be completely dried. Si sol in cold $w$; insol in alc and eth. Decomps explosively at 115°.


Percorinit (Percorinite). A blasting expl which replaced Coronit in stone quarries and ore mines: K perchlorate 65, NG 5, aromatic nitrocompds 25, and vegetable meal 5% (See also Perkorinit) Refs: 1) Bebie (1943), 116 2) PATR 2510 (1958), Ger 129-R 3) F.A. Warren et al, "Chlorates and Perchlorates, Their Manufacture, Properties and Uses", NavOrdRept 7147, Vol 1 (1960), 205

Percussion. The act of striking one body against another with a sharp blow. As some exps, such as MF or LS: are very sensitive to such a blow (shock or impact), they may be expld (or ignited) by such action. In this case, the term "percussion" can be applied to initiation or priming by such action, as well as to the expln (or deflagration or ignition) caused by percussion.

Percussion or Explosive Bullet. A bullet provided with a percussion cap which, on impact, expls a powder charge inside the bullet.
Percussion Cap. (See under Cups, Percussion or Primer; and Caps in Vol 3, C577; and Anvil of a Percussion Primer in Vol 1, A473-L)

Percussion Fuze. See Vol 4, D882-R

Percussion Gun. See under Percussion Principle in Vol 4, D755-L

Percussion Lock. A firearm mechanism in which a cap loaded with a detonating mixt is fitted over a pierced nipple and exploded by the blow of the falling hammer. The flash of the exploding cap is carried to the charge. Its development followed that of the flintlock (See Vol 6, F107-R), and its use was widespread by the middle of the nineteenth century. The US Army adopted percussion rifles and muskets in 1841–42, and by 1842 all British Brown Bess muskets were converted to percussion fire. Also see under History of Development of Military Detonators, Igniters, Primers and Other Initiating Devices in Vol 4, D753-R to D756-R


Percussion Powder. Any compd or mixt which can be easily fired by percussion. The first mixts of this type were invented by a Scotch clergyman, A. Forsyth. See Vol 4, D755-R and Vol 6, F232-R

Percussion Primer. See under Primer, Percussion in this Vol

Perdite (Perdite). Ger perchlorate expls of varying compn, introduced during WWI as replacements for the Corps of Engineers Explosive (Pioneer munition), Donarit (see Vol 5, D153). A compn contg K perchlorate 56, DNB 32 and DNN 12% was used in trench mortar shells and mines. Stettbacher (Ref 2) referred to it as “Deutscher Geissbarer Minensprengstoffe” (Ger castable mine expl)

A Compn contg AN 72, K perchlorate 10, wood meal 3, and a eutectic mixt of DNT and TNT 15%, was used as a demolition charge and for loading bombs and trench mortar shells. Its d was 1.20–1.25g/cc; Trauzl test value, 370–380cc; sensitivity to initiation, required at least a No 3 cap for detonation

Refs: 1) Naoum, Expls (1927), 132–3
2) Stettbacher (1933), 316
3) Pepin-Lehalleur (1935), 352
4) Davis (1943), 364
5) A. Pérez Ara (1945), 243
6) Urbański 3 (1967), 264

Perforated Grains (Propellants). See under Cannon Propellant or Cannon Powder in Vol 2, C30 to C31

Performance of Explosives or Propellants. The best way to estimate their performance is to conduct “practical” tests by actual firings (see Performance Tests, Practical). As these tests are rather expensive and require large “Proving Grounds” for their execution, it is common to conduct preliminary testing by any of the following indirect methods:

<table>
<thead>
<tr>
<th>TNT</th>
<th>PA</th>
<th>Tetryl</th>
<th>Pentryl</th>
</tr>
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<tr>
<td>14.8</td>
<td>16.4</td>
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<td>18.5</td>
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Compression of Pb cylinder in mm
Relative percussion 1.00 1.11 1.12 1.25
effect (TNT=1.00)

The test was conducted in the same manner as described by Munroe & Tiffany (Ref 1)

Note: Earlier investigators such as Kast, Hess, Vennin, Burlot and Lécorché regarded this test as being indicative of relative brisance

Refs: 1) C.E. Munroe & J.E. Tiffany, USBur-Mines Bull 346 (1931) 2) LeRoy V. Clark, IEC 25, 1389 (1933)

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Refs: 1) C.E. Munroe & J.E. Tiffany, USBur-Mines Bull 346 (1931) 2) LeRoy V. Clark, IEC 25, 1389 (1933)
**Brisance** (shattering power). Measured by a series of tests which determine the explosive’s ability to crush sand, fragment steel pipe, or deform solid Pb cylinders. The results of these tests are recorded as the weight of sand crushed, the number and size of pipe fragments produced, or the distance the cylinder is deformed.

**Power.** Is a measure of the max press developed by detonation and the rate at which this pressure is released. The Ballistic Pendulum used for testing expl power consists of a mortar (suspended as a pendulum from knife-edges) in which an expl sample is detonated to expel a heavy shot from the mortar and cause the suspended mortar to recoil. The recoil of the mortar is proportional to the propulsive force of the expl, and the arc of swing is registered in cm and compared with that obtained with a standard expl such as TNT.

**Detonation Velocity.** The speed at which the detonation wave travels thru the expl, or the rate of chemical reaction of the detonation process. High-speed photographic testing has determined that this reaction is of the order of a few microseconds, showing that as the detonation wave progresses the area behind the wave undergoes a chemical change, while the area or material ahead of the detonation wave remains unchanged until the wave passes thru it. Detonation velocity can be measured with high-speed streak cameras, spectrometers, or electric counters which record the make-break cycle of the detonation wave causes in an electric circuit.

**Sensitivity.** Friction sensitivity, as detd by the Friction Pendulum app, consists of dropping a pendulum with a 20-kg steel- or fiber-faced shoe one meter so that it swings across a grooved anvil into which a sample of expl has been spread. The passing of the shoe over the sample is recorded by the number of snaps, cracklings, ignitions and expls that occur. The steel-faced shoe will often produce snaps, crackles, or detonations in expls that withstand the fiber-faced shoe.

Impact sensitivity can be expressed by denoting the min height of drop at which a standard test wt (2 or 10kg) will detonate an expl sample.

Shock sensitivity of an expl can be gaged by subjecting a sample to the impact of a rifle bullet. In this test the caliber and type of bullet and the manner in which the expl sample is contained or positioned during the test can be varied. Confinement generally enhances the probability that an expl will detonate in the rifle-bullet test.

Detonation sensitivity determines if an expl possesses the sensitivity necessary for it to react predictably from the action of the initiating medium designed to produce detonation. To determine the detonation sensitivity of an expl, standard test detonators of graded strength ratings from 1/2 to 16 are utilized. Their strength ratings are controlled by varying the type and wt of charge, and equating the detonators to 90/10 MF/K chlorate or PETN/LA detonators which specify the following charges:

<table>
<thead>
<tr>
<th>Test Detonator No.</th>
<th>Weight of Charge, 90/10 MF/K chlorate compn, g</th>
<th>Weight of Charge, PETN/LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>¼</td>
<td>0.26</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>0.30</td>
<td>–</td>
</tr>
<tr>
<td>1½</td>
<td>0.35</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>0.40</td>
<td>–</td>
</tr>
<tr>
<td>2½</td>
<td>0.47</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>0.54</td>
<td>–</td>
</tr>
<tr>
<td>3½</td>
<td>0.59</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>0.65</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>0.80</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>1.50</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>2.00</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>–</td>
<td>1.20g PETN/0.35g LA ignition mixt</td>
</tr>
<tr>
<td>16</td>
<td>–</td>
<td>1.50g PETN/0.35g LA ignition mixt</td>
</tr>
</tbody>
</table>

Grades of commercial expls not cap-sensitive and most military expls which cannot be detonated with a No 6 commercial blasting cap must be tested with detonators of No 8–16 strength in order to detn their sensitivity. Less sensitive expls, ie, Nitrocarbonitrates (ANFO), expl slurries, and Nitrocarbonitate slurries, necessitate the use of extremely large initiators of 3–10g for ANFO mixts, to 50g or larger for the less sensitive slurries in order to detn basic sensitivity. Normally, initiation test charges larger than 3g are made of Pentolite, Comp B, or other high-strength expls, which, in turn, are detonated by a blasting cap.

To the above tests can be added: explosion,
or ignition temp; sensitivity to flame, temp developed on expln or combustion; thermal stability; mp; bp; loading d; "colorific power", etc.

In terms of the application of these tests as yardsticks for specific expl usage, the following examples are given:

1) If an expl is intended as a bursting charge in general purpose shells, there would be required high brisance, high power, high detonation velocity, and low sensitivity to impact, friction and shock (TNT, PA, Comp B, Pentolite, etc would be suitable)

2) If an expl is to be used for APS (armor-piercing shell) application, the same requirements as above are pertinent, except that the impact sensitivity should be very low (Explosive D, TNT desensitized with wax, etc, would be suitable)

3) If an expl is to be used as a booster, the same requirements as in (1) are applicable, except that the impact sensitivity should be higher (Tetryl, PETN, RDX, cryst PA, Nitromunite, etc, would be suitable)

All of the above expls should also possess high thermal stability

4) If an expl is intended for use in primers, then its brisance and power may be lower than for groups (1), (2) and (3), but it should possess low sensitivity to impact and friction and should produce a hot flame in order to ignite a charge of proplnt or a delay train

5) In the case of initiating expls, the requirements are the same as in (4) except that a hot flame is not required, but rather that it produce a shock wave strong enough to detonate a HB such as Tetryl, PETN, RDX, PA, TNT, etc

6) In the case of blasting expls to be used in coal mining applications, brisance should be low (to avoid breaking the coal down too finely); power and detonation velocity should also be low, but the gas volume evolved on expln should be high so that the so-called "heaving power" will be great. If mines are gaseous, it is required that the temp developed on expln be sufficiently low so as not to cause ignition of firedamp

7) With regard to proplnts, brisance, power and detonation velocity are not tested. It is, however, necessary to determine the burning rate, press developed on burning, vol of gas evolved, calorific value, thermal stability, etc. If one is concerned with gun barrel life, the calorific power should be low


Performance Tests, Practical. Any test based on the employment of an expl or ammo item under actual operating conditions may be included in this category. For example, a blasting expl can be tested by burying a weighed sample deep in the ground and then firing it. The effect caused by the expln of the sample is compared with that produced by an equal weight of standard expl fired under the same conditions. This is called the "Cratering Effect Test" (Refs 1 & 2)

In testing proplnts, several charges can be fired, varying the weight of charges, etc, until the desired performance is achieved

In the testing of demolition expls, eg, those intended for the destruction of rails, various charges can be detonated against an explt rail until the minimum amount of charge required is established

In testing penetration of armor, etc, by various projectiles, they can be fired against armor plate of varying thickness and compnt until the maximum depth of penetration is der

In testing the performance of expls used for bursting charges, the so-called "fragmentation test" (see Vol 6, F180–181) gives fairly accurate results. This test can also be used to determine the performance of metals used in the construction of various projectiles


Periodic Acid and Periodates

Periodic Acid. HIO₄·2H₂O, mw 227.96, monoclinic hygr crysts, loses 2H₂O at about 100°, mp 122°, decomp at 130–140°. Sol in w and alc; sl sol in eth (Refs 5 & 6). Prepbd by electrolytic oxidation of iodic acid or from Ba periodate according to the equation
Ba$_3$H$_4$(IO$_6$)$_2$+6HNO$_3$ → 2H$_2$IO$_6$+3Ba(NO$_3$)$_2$

Ref: 1. Periodic acid is highly toxic, and is dangerous in contact with organic materials (Ref 7). In periodic-dimethyl sulfoxide oxidizing systems, violent explns can occur if the concn of periodic acid is too strong. For example, in oxidizing glycopyranosides an expln took place at a 1.5N concn of the periodic acid (Refs 2, 3 & 4).

Refs: 1) J. Willard, InorgSynth 1, 172 (1939)
2) Anon., C&EN 44 (15), 48 (1966)
4) Ibid, JACS 90 (7), 1924 (1968)
5) Merck (1968), 799
7) Sax (1975), 832

Ammonium Periodate (Ammonium meta-Periodate). NH$_4$IO$_4$, mw 208.96, color crys., mp explos., d 3.056g/cc at 18/4°C. Was prep by C.F. Rammelsberg in 1868 and by T.V. Barker in 1908 (Refs 1 & 2) by neutralizing periodic acid with aq ammonia. Sax (Ref 6) lists it as an expl and advises great care in its storage and handling because a simple abrasion, or impact at ordinary temps, is sufficient to detonate it violently. A serious expln occurred on simply scooping the material from one container to another (Ref 3). Ellern (Ref 5) reports that the metaperiodates (MeIO$_4$) can decomp with expl violence when strongly heated, and Remy (Ref 4) states that ammonium periodate may expl even on gentle friction, eg, when touched with a spatula. If stored, it must be kept in a cool, isolated area away from fire hazards, excessive vibration and shock. It can be disposed of by dissolving in w.

Refs: 1) T.V. Barker, JCS 93, 17 (1908)
2) Mellor 2 (1922), 386–95 & 406–18
3) G.F. Smith, C&EN 29, 1770 (1951)
5) Ellern (1968), 288
6) Sax (1975), 394

Potassium Periodate. (Potassium meta-Periodate). KIO$_4$, mw 230.00, color tetragonal crys., mp 582°C, explos at 1076°F (Ref 3), bp $-$O$_2$ at 306°C, d 3.618g/cc at 15/4°C. Sl sol in w, v sl sol in KOH. Can be prep by the oxidizing action of chlorine on a hot soln of K iodate and an excess of KOH, or by the electrolysis of K iodate. K periodate is highly toxic, a strong irritant to tissue, and a fire risk when in contact with organic materials.

Refs: 1) Mellor 2 (1922), 386–95 & 406–18
2) CondChemDict (1971), 724–L
3) Sax (1975), 1051

Perkins Explosive. A primary mixt patented in Engl in 1870 contg amorph P, metallic sulfides (such as antimony sulfide), and K chloride or nitrate.

Ref: Daniel (1902), 609

Perkoronit. Ger perchlorate expls of varying compn, extensively used during and after WWI for blasting purposes (especially in ore mines and quarries).

According to Naoum (Ref 1), the original Perkoronits were: 1) K perchlorate 77, m-DNT 10, woodmeal 3, powdered coal 1, paraffin 5 & NG 4%; OB to CO$_2$ +0.9% and Trauzl value 285cc; 2) K perchlorate 68, AN 10, DNT 16, woodmeal 1, naphthalene 1 & NG 4%; OB to CO$_2$ +11.1% and Trauzl value 265cc.

After WWI, these expls were replaced by the following two, manuf by Dynamit-A-G

<table>
<thead>
<tr>
<th>Components and Properties</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>K perchlorate</td>
<td>58</td>
<td>59</td>
</tr>
<tr>
<td>Amm nitrate</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>DNT+TNT+vegetable meal</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>NG (nitroglycerin)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Oxygen Balance to CO$_2$, %</td>
<td>+2.2</td>
<td>+1.8</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.58</td>
<td>1.52</td>
</tr>
<tr>
<td>Velocity of Deton, m/sec</td>
<td>5000</td>
<td>4400</td>
</tr>
<tr>
<td>Trauzl Test, cc</td>
<td>340</td>
<td>330</td>
</tr>
<tr>
<td>Pb Block Crushing, mm</td>
<td>20.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Requires for initiation, min</td>
<td>No 3 cap</td>
<td>No 3 cap</td>
</tr>
<tr>
<td>Gap Test, cm</td>
<td>6.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Heat of Explosion, kcal/kg</td>
<td>1170</td>
<td>1160</td>
</tr>
<tr>
<td>Temp of Explosion, °C</td>
<td>3145</td>
<td>3115</td>
</tr>
</tbody>
</table>

These expls were highly brisant, being about equal in that respect to the best chlorate expls. There were also some “Perkoronits” that did not contain AN.


**Permanganates**

**Ammonium Permanganate.** NH₄MnO₄, mw 136.97, mp explos (see below), d 2.2088/cc at 10°. Long, reddish-purple needles; rhombic crystals (crystals become steel-grey in storage, presumably due to surface reactions). Sol in cold w, decmpd by hot w. Was prep'd by E. Mitscherlich in about 1824 (Refs 1 & 2) by treating AgMnO₄ with an equiv quantity of NH₄Cl, filtering the liq and evaporap to crystals. H. Aschoff (Ref 3) used the same process, while R. Böttger (Ref 1) prep'd it from Ba(MnO₄)₂ and NH₄SO₄. Christiansen (Ref 4) modified Böttger's method. Since NH₄MnO₄ decomp in hot w, as used in the Christiansen method, Bircumshaw and Taylor (Ref 7) proposed the following modification: KMnO₄ (40g) was dissolved in boiling w (400g), NH₄Cl (110g) added, and the hot soln immediately filtered thru a sintered glass funnel (to remove Mn oxides) into a container placed in a cooling mixt. The crystals were recrystd twice from hot w in the same manner.

Although most handbooks give its expln temp as 60°, more recent work (Ref 7) has shown that when 0.02g samples of NH₄MnO₄ were heated in air, they expld at 96° only after heating (induction period) for 600–700 seconds, while at 117° it required from 80 to 110 seconds. No expln at 60° was reported. When small samples were heated under confinement (immersed in an inert oil), they expld at 99.5° after about 10 minutes, but required 250 mins to expld at 70°.

Amm permanganate decomp slowly in storage even at ordinary temps, forming manganese oxides. After 3 month storage the sample was only 96% pure, and after 6 months it as-

**Potassium Permanganate.** KMnO₄, mw 158.03; dark purple or bronze-like, odorless crystals; sweet with astringent taste; stable in air; mp, decomp at 240° with evolution of O₂; d 2.7032 g/cc. Sol in w, acet and methanol; decomp by alc. Can be prep'd by (a) oxidation of the manganate in an alkaline electrolytic cell; (b) treating a hot soln of the manganate with CO₂ on cooling, the soln deposits crystals of the permanganate (Refs 6 & 7).

**Hazard.** K permanganate is a powerful oxidizing agent. It can expld in contact with organic materials, especially alc, ether, glycerin and combustible gases or with sulfuric acid.

Bretherick (Ref 8) details the following incidents with original references:

**Acetic acid or Acetic anhydride.** Cooling is necessary to prevent possible expln from contact of K permanganate (or the Ca or Na salts) with acetic acid or its anhydride.

**Aluminum carbide.** Incandescence on heating.

**Ammonia, Sulfuric acid.** Ammonia is oxidized with incandescence in contact with the per-
manganic acid formed in the mixt.

Ammonium nitrate. A mixt of 0.5% K permanganate with an AN expln caused an expln 7 hours later. This was due to formation and exothermic decompn of Amm permanganate, leading to ignition.

Antimony or Arsenic. Sb ignites on grinding in a mortar with the solid permanganate, while As explds.

Glycerol. Contact of glycerol with solid K permanganate caused a vigorous fire.

Hydrochloric acid. During prepn of chlorine by addition of the concd acid to solid permanganate, a sharp expln occurred on one occasion (contamination of the acid with sulfuric acid could have produced permanganic acid).

Hydrogen peroxide. Contact of H₂O₂ soln from a broken bottle with previous packages of permanganate caused a violent reaction and fire.

Hydrogen trisulfide. Contact with solid permanganate ignites the lg sulfide.

Non-metals. A mixt of C and K permanganate is not friction sensitive, but burns vigorously on heating. Mixts with P or S react explosively on grinding and heating, respectively.

Sulfuric acid, Water. Addition of concd sulfuric acid to the slightly damp permanganate caused an expln. This was attributed to formation of permanganic acid, dehydration to dimanganese heptoxide and expln of the latter, caused by heat liberated from interaction of sulfuric acid and moisture. A similar incident was reported previously, when a soln of K permanganate in sulfuric acid, prepd as a cleaning agent, expld violently.

Titanium. A mixt of powdered metal and oxidant explds on heating.

Wood. Contact between solid K permanganate and wood, either in the presence of moisture or of mechanical friction, may cause a fire.

Ref 9 adds the following hazardous reactions without references:

Sulfur, Tin. Expln results on heating with K permanganate to 170° or higher.

Ethanol plus Sulfuric acid. Ignition with flashing on contact with K permanganate.

Acids plus concd Sulfuric acid. Ignition on contact with K permanganate.

Iron. Combustion on percussion of mixt with K permanganate.

Ether, Alcohol, Paper, Turpentine oil plus Sulfuric acid. Ignition on contact with K permanganate.

Ref 10 adds hazardous reactions between K permanganate and Al carbide, As, dimethyl sulfoxide, hydroxylamine, and polypropylene, which are supported by references.

Toxicity. Sax (Ref 11) lists K permanganate as being highly toxic by ingestion, inhalation, or as an irritant. Ref 4 gives a lethal dose 50% kill level (orally in rats) of 1090 mg/kg, (subcutaneous in mice) of 500 mg/kg.

Uses. According to Daniel (Ref 2), K permanganate, as well as other permanganates were used as oxidizing agents in expln comps. However, there was no advantage over materials such as K nitrate, AN, K perchlorate, etc (also see Ref 3).

Davis (Ref 4) reports its use in pyrots as a "flash report" in the mixt 3p K permanganate/2p Al.

Fielder (Ref 4) used it in a lg expln prepd by soaking a mixt of 70p K chloride/30p K permanganate in a lg consisting of 80p NB/20p turpentine.

Ellern (Ref 5) comments on its use in pyrot delay comps and heating devices.

Specification. A US Military Specification (MIL-P-11970B, 23 Aug 1973) entitled, "Potassium Perchlorate, Technical Grade", covers the Dept of Defense requirements. They state that the material shall be in the form of dark purple crystals and shall assy at not less than 97.0% K permanganate by titration into Na oxalate/dil sulfuric acid soln.

Silver Permanganate. \( \text{AgMnO}_4 \), mw 226.81; dark violet, monoclinic crystals; mp, deflagrates at about 135°; d 4.27g/cc; decomps in light. Si sol in cold w, decomp by hot w or alc. Can be prep'd by thoroughly mixing a 5% K permanganate soin with an equiv quantity of 5N Ag nitrate soin. The resulting ppt is filtered, washed with ice cold w, and dried in a vacuum desiccator over sulfuric acid. Purity of the product is 99.5–100%. Ref 3 terms it a dangerous expln risk which may detonate if shocked or heated.

By adding concd ag ammonia to a 1M K permanganate soin in w at 10°, and adding one mole of Ag nitrate dissolved in 10 times its wt of w, T. Klobb (Ref 1) obtained

Silver Diamminoperpermanganate, \( \text{AgMnO}_4 \cdot 2\text{NH}_3 \); violet rhombic plates; sparingly sol in cold w, more sol in hot w. It expld on percussion; decomps slowly on standing.


Sodium Permanganate. NaMnO\(_4\).3H\(_2\)O, mw 194.98; purple to reddish-black crystals or powder; mp 170°, decomp; d 2.47g/cc. Very sol in w, decomps in alc. Can be prep'd by passing a current of chlorine or ozone thru an ag soin of Na manganate. The soin is then concd and crystd. Na permanganate is a strong oxidizing agent, highly toxic, and is a dangerous fire risk in contact with combustible materials.


Complex Explosive Salts of Permanganate.

In addition to Ag diamminoperpermanganate, described above under Ag permanganate, there are other expl ammino-comps, eg:

Cadmium Tetramminoperpermanganate.
\( \text{Cd(MnO}_4\).4\text{NH}_3 \). It was prep'd by T. Klobb by saturating a soin of K permanganate with ammonia, and adding a soin of a Cd salt. In a few days, the black crystals turned to a brown mass, which detonates on percussion.

Cobaltic Hexamminoperpermanganate.
\( \text{[Co(NH}_3\).6](\text{MnO}_4\).3 \). Black tetrahdryl crystals, sol in cold w, sol in hot w with decomp.

Expls on heating or on being struck. It was prep'd by T. Klobb and E. Wilke-Dörfurt by mixing a warm concd soin of one mole of cobaltic hexamminochloride with 12 moles of K permanganate.

Cobaltic Hexamminodichloroperpermanganate.
\( \text{[Co(NH}_3\).6]\text{Cl}_2(\text{MnO}_4) \). Black crystals, appearing red or brown in transmitted light. Very unstable; decomp by w; detonates on rapid heating. Was prep'd by treating a warm soin of 8 moles of cobaltic hexamminochloride with a soin of 1 mole of cobaltic hexamminoperpermanganate, then filtering rapidly and allowing to cool.

Ref: Mellor 12 (1932), 335–6

Perfluorosuccinimamide-Lithium Aluminum Hydride (Danger of Explosion). In an attempt to reduce perfluorosuccinimamide to the corresponding diamine, it was added to an ether soin of lithium aluminum hydride in a nitrogen atm. Hydrolysis was then attempted, but as a second drop of w was added, a violent expln and ether fire resulted. It was shown that the diamide and the lithium aluminum hydride reacted to give an unstable complex which detonated at room temp.

Ref: T. S. Reid & G. H. Smith, C&EN 29, 3042 (1951) & CA 46, 3279 (1952)

Perform. Another name for 3,7-Dinitrosotetrazazaboracyclo[3,3,1]-nonane. See Vol 5, E91-L

Performance vs Constitution of Explosives. The following discussion is taken from Ref 9, published under the title "Classification of Explosives":

Expls may be classified both from the chemical point of view and according to their uses. From the chemical viewpoint we distinguish between chemical individual substances and mixts. The former are divided into: (1) nitro comps, (2) nitric esters, (3) nitramines, (4) derivatives of chloric and perchloric acids, (5) azides, and (6) various comps capable of producing an expln, for example fulminates, acetylides, nitrogen rich comps such as tetrazene, peroxides and ozonides, etc.

Individual substances are expl if their mole-
cules contain groups which confer upon them exp1 props. The first attempt at a systematic approach to the relation between the exp1 props of a molecule and its structure was made by van't Hoff (Ref 1). He pointed out, that in the molecules of exp1 compds the following groups were present:

1. O = O in peroxides and ozone and ozonides
2. O = Cl in chlorates and perchlorates
3. N = Cl in nitrogen chloride
4. N = O in nitro compds, nitric acid esters and salts
5. N = N in diazo compds, hydrazoic acid, its salts and esters
6. N = C in fulminates and cyanogen
7. C = C in acetylene and acetylides

A further effort to establish a relationship between exp1 props and structure has been made more recently by Pletz (Ref 7). He proposed a theory of "explosophores" and "auxexploases". According to Pletz the exp1 props of any substance depend upon the presence of definite structural groupings, called explosophores. The auxexploases fortify or modify the exp1 props conferred by the explosophore. Pletz divided all exp1s into eight classes containing the following groups as explosophores:

1. \(-\text{NO}_2\) and \(-\text{ONO}_2\) in both inorganic and organic substances
2. \(-\text{N} = \text{N} - \) and \(-\text{N} = \text{N} = \text{N} -\) in inorganic and organic azides
3. \(-\text{NX}_2\), for example in \(\text{NCI}_3\) (X = a halogen)
4. \(-\text{N} = \text{C}\) in fulminates
5. \(-\text{OCIO}_2\) and \(-\text{OCIO}_3\) in inorganic and organic chlorates and perchlorates respectively
6. \(-\text{O} = \text{O} -\) and \(-\text{O} = \text{O} = \text{O} -\) in inorganic and organic peroxides and ozonides respectively
7. \(-\text{C} = \text{C}\) in acetylene and metal acetylides
8. \(-\text{M} = \text{C}\) metal bonded with carbon in some organometallic compds

Although this classification is in principle correct, the distinction between the terms "explosophore" and "auxexploase" is very vague and of little practical value.

A further step in the classification of exp1s was made by Lothrop and Handrick (Ref 4). They collected and classified all the available information on the performance of exp1s and related it to four factors: oxygen balance, "plosophoric" groups, "auxexploasive" groups, and heat of exp1n.

A plosophore has been defined as a group of atoms which is capable of forming an exp1 compd on introduction into a hydrocarbon. According to these authors there are two classes of plosophores differing sharply in effectiveness and consistency in producing power. Hence it is suggested that these be called "primary" and "secondary" plosophores. Primary plosophores include nitrate esters, aromatic and aliphatic nitro groups and the nitramine group. The secondary plosophores that comprise the remainder include such groups as azo, azide, nitroso, peroxide, oxonide, perchlorate, etc. If more than one type of these groups is present in a molecule, it may be named a hybrid according to Lothrop and Handrick. Groups which do not themselves produce exp1 props, but may influence them are called auxexploasives by these authors. We may quote hydroxy, carboxyl, chlorine, sulfur, ether, oxygen, amine, etc. as examples of such groups.

Although the classification of groups existing in exp1 molecules suggested by Lothrop and Handrick may be accepted, their far-reaching postulations concerning a close relation between the oxygen balance and performance of exp1s aroused strong criticism (Ref 6). It is known that the oxygen present, for example, in carboxyl or hydroxyl groups, has little effect on the performance of an exp1. This is due to the high heat of formation of \(\text{C} = \text{O}\) and \(\text{C} = \text{O} - \text{H}\) bonds. On the contrary, the low (negative) heats of formation of \(\text{N} = \text{O}\) and \(\text{C} = \text{C}\) bonds are of great significance in relation to the performance of exp1s.

That is the reason why the performance of Picric Acid (trinitrophenol) is only very slightly higher than that of Trinitrobenzene and why the performance of Trinitroanisole is much the same as that of Trinitrotoluene.

The low value of the exp1 power of oxygen atoms bonded with carbon and hydrogen atoms in such a group as \(\text{COOH}\) had already been stressed by Stettbacher (Ref 2), who also pointed out that an exception is provided by peroxides and ozonides which form exothermic bonds that considerably enhance exp1 performance.

However, the slightly better performance of
Picric Acid compared with Trinitrobenzene is probably the result of the former’s greater ability to detonate. The ease of detonation of Picric and Stypnic acids as compared with Trinitrobenzene is well known. D. Smoleński and W. Czuba (Ref 8) recently pointed out that Dinitrophenol detonates more readily than Dinitrobenzene.

It is also well known from the classic work of L. Wöhler and Wenzelberg (Ref 3) that the sensitivity to impact of aromatic nitro compounds increases with increase in the number of substituents for a given member of the nitro groups. Refs: 1) H. van’t Hoff, according to H. Brunswig Explosivat, Barth, Braunschweig (1909), 17. 2) A. Stettbacher, AngChem 30, 269 (1917) & CA 12, 3011 (1918); Ibid, “Die Schiess-und Sprengstoffe”, Barth, Leipzig (1919) & CA 14, 468 (1920) 3) L. Wöhler & O. Wenzelberg, AngChem 46, 173 (1933); not found in CA 4) W.C. Lothrop & G.R. Handrick, ChemRevs 44 (3), 419-445 (1949) & CA 43, 6416 (1949) 5) K. Singh, JsClindResearch(India), 10A, 406-19 (1951) [A review with 27 refs on the relation between chemical constitution and performance of organic expl compds] 6) A. Schmidt, ChimInd 67, 253 (1952) & CA 46, 5843 (1952) 7) V. Petz, ZhObschKhimi(IGenChem) 5, 173 (1953); not found in CA 8) D. Smoleński & W. Czuba, ZesztyNauk-PolitWrodawskiej, Chemia 7, 3 (1955) 9) Urbanski 1, 1-3 (1964)

**Performic Acid.** (Peroxyniformic Acid, Permethanoic Acid, Formylhydroperoxide). ACOOOH, mw 62.03, the 90% soln is a colorless liq, is prone to expid on contact with metals, their oxides, reducing substances, or on distn. A 90% soln is obtained when a mixt of 20g formic acid, 25g 100% hydrogen peroxide and 6.5g sulfuric acid is allowed to interact for 2 hrs and is then distd. Misc with w, alc, eth; sol in benz and chlf (Refs 6 & 8)

Performic acid solns are unstable and undergo a self-accelerating exothermic decompn at ambient temp (Ref 2). An 80% soln expid at 80-85°C (Ref 1). A small sample of the pure vacuum distd material cooled to below -10°C expid violently when the flask was moved (Ref 5). Although the acid has occasionally been distd, it is an extremely dangerous operation (Ref 7).

With regard to metals or oxides, the violence of reaction depends on concn of the performic acid as well as the scale and proportion of the reactants. The following observations were made (Ref 1) with additions of 2-3 drops of about 90% performic acid. Ni powder becomes violent; Hg, colloidal Ag and Th powder readily cause explns. Zn powder causes a violent expln immediately. Fe powder (and Si) are ineffective alone, but a trace of Mn dioxide promotes deflagration. Ba peroxide, Cu oxide, impure Cr trioxide, Ir dioxide, Pb dioxide, Mn dioxide, and V pentoxide all cause violent decompn, sometimes accelerating to expln. Pb oxide, trilead tetroxide and Na peroxide all cause an immediate violent expln.

Impure C and red P are oxidized violently, and Si, promoted by traces of Mn dioxide, is oxidized with ignition (Ref 1).

Formaldehyde, benzaldehyde and aniline react violently with 90% performic acid (Ref 1). An unspecified organic compd was added to the acid, and soon after the initial vigorous reaction had subsided, the mixt expid violently (Ref 3). Reaction with alkenes is vigorously exothermic, and adequate cooling is necessary. Reactions with performic acid can be more safely accomplished by the slow addition of hydrogen peroxide to a soln of the compd in formic acid (Ref 4).


**Perminite.** See under Permonit in this Vol.

**Permissible or Permitted Explosives.** In many coal mines there is a continual evolution of methane (firedamp) into the air of the workings.
The methane is trapped in the coal or rock, often in pockets within the veins, and is sometimes of relatively high pressure. It is usually of fairly high purity, containing only minor amounts of other hydrocarbons and N₂. Methane, when mixed with air in proportions between 5 and 14%, forms an expl mixt. In gassy mines, therefore, there is always the danger that a mixt may be formed which, if ignited, can cause serious damage and loss of life. In coal mines, also, there is further danger in that the working of the coal produces coal dust. Coal dust, when mixed with air, gives a mixt which when suitably ignited can undergo a dust expln. Indeed, if an expln of firedamp (or coal dust) occurs, the wave produced can stir the dust lying in the mine into the air, producing a mixt which can lead to further propagation and devastating expln. In the history of coal mining there have been many examples of both firedamp and coal dust explns, and the latter in particular have led to serious loss of life (Ref 2).

These frequent coal mine disasters led, early in the HE industry, to the careful regulation of the expls that could be permitted for use in coal mining. Expls allowed for use in gassy and dusty US coal mines are called permisibles; those in England and Canada are called permitted expls; in France, explosifs antigrisoutex; in Belgium, explosifs S.G.P. (sécurité, grisou, poussière); and in Ger, schlagwettersichere Sprengstoffe. In US permisibles, AN has from the beginning been an important safety ingredient as regards ignition of coal gas and dust. It owes its safety qualities in this regard to the low expl temp in expls containing large percentages of AN (Ref 1).

For an in-depth coverage of this topic, the reader is referred to Vol 3, C368-R to C378, under Coal Mining Explosives, Testing for Permissibility, and Vol 3, C444-R to C459-R under Coal Mining Explosives, Permissible

Refs: 1) Cook (1958), 10–11 & 15–16
2) S. Fordham, “High Explosives and Propellants”, Pergamon, NY (1966), 81–97
3) Ubański 3 (1967), 461–89

Permonite (Permonit, Perminite). Gcr blasting expls based on perchlorate, manufd by the Sprengstoff A-G Carbonit before WWI. Typical formulations were: K perchlorate 30 to 37.5, AN 30 to 37.5, K or Na nitrate 7, nitrobody (such as TNT) 10 to 25, woodmeal 3, cereal meal 4, and a mixt of glue, glycerin and gelatin 1% (Refs 2 & 4).

Escales (Ref 1), Marshall (Ref 2) and Barnett (Ref 3) give the compn of Permonite which was on the permitted list in Engl before WWI as K perchlorate 31–34, NG 3–4, collagen cotton 0.5 to 1, AN 39–43, TNT 11–13, starch 5–9, woodmeal 1.5–3.5, and jelly (mixt of 1p glycerin and 3.5g gelatin) 1.5–3.5%. Gap test, 80mm; Trauzl test, 365cc; Sensitivity to Impact, 20cm with a 2kg wt. This expl failed to pass the Rotterdam test.

Marshall (Ref 2) gives the compn and properties of the following Permonites:

**Permonit I or Gasteins Permonit.** K perchlorate 30, AN 40, Na nitrate 7, TNT 15, flour 4, woodmeal 3, and jelly 1%. Gap test, 70mm; Trauzl test, 320cc; Detonation Velocity, 3470m/sec; Sensitivity to Impact, 70cm with a 2kg wt.

**Permonit S.G.P. (Used in Belg).** K perchlorate 24.5, NG 6, AN 29, TNT 25, flour 4, woodmeal 3, and jelly 1%. Gap test, 100mm; Trauzl test, 255cc; Detonation Velocity, 2326m/sec; Sensitivity to Impact, 80cm with a 2kg wt; limit charge, 900g, equiv to 575g of Dynamite No 1

*Note: The Gap test (Influence or Propagation test) mentioned above consisted of ascertaining the distance over which the detonation is conveyed from one 30cm cartridge loaded with a test formulation to another lying on the ground.*

**Permonit of Bichel.** The following expl was patented in Fr in 1905 by C.E. Bichel, and was called Permonit (Ref 1, p 185): Amm perchlorate + K chloride mixt 70–80, NG 4–10, and TNT 6–10%

**Permonit A.** Escales (Ref 1, p 185) gives the following compn: K perchlorate + AN, max 54; gelatinized NG, max 4; the balance consisting of nitroaromatic compds (of which TNT, max 20%) and woodmeal

Refs: 1) R. Escales, “Chloratsprengstoffe”, Leipzig (1910), 105, 150 & 185
2) Marshall 1 (1917), 384 & 2 (1917), 493
3) Barnett (1919), 111–112
4) Ullmann 4, 2nd Ed (1926), 788–9
5) A. Pérez Ara (1945), 218
Perintra. A perchlorate expl authorized in Engl before WWI, but never manufd. It contained Amm perchlorate 40, Na nitrate 30, solid TNT 10, liq TNT 10, and Al powder 10%
Ref: Barnett (1919), 112

Perintryl Fluoride. See under Nitrogen Tri-oxyfluoride in this Vol

PEROXIDES

Peroxide compds, both inorganic and organic (see below under each of these sections), are usually described as compds whose structures include the peroxy-group, $\text{O}^\bullet\text{-O-}$. The electronic structure of this $\text{O}_2^{2-}$ ion is depicted in Fig 1. According to Vol'nov (Ref 1) the $\text{O}_2^{2-}$ ion has an even number of electrons, 14, and the symbol for the ground state of this ion is $\Sigma$, which is in agreement with the diamagnetism and absence of color which characterize compds contg this ion.

\[
\text{O}_2^{2-}
\]

Fig 1. Electron Structure of the $\text{O}_2^{2-}$ ion

The molecular orbital notation for the $\text{O}_2^{2-}$ ion is $\{\text{KK}(\text{Z}\text{O})^2(\text{Y}^\text{O})^2(\text{X}^\text{O})^2(\text{Wm})^4(\text{Vn})^4\}$. The $\text{O}_2^{2-}$ ion represents an ellipsoid of rotation with the major axis 4.19 Å long. The radius of the $\text{O}^-$ ion in the $\text{O}_2^{2-}$ ion is 1.35 Å. The O–O bond length is (about) 1.49 Å. The major semi-axis of the $\text{O}_2^{2-}$ ion is, therefore, equal to 2.09 Å. The minor semi-axis (or transverse radius) is 1.23 Å. The bond dissociation energy of O–O in hydrogen peroxide is 1.5 eV, which is approx (reported from 20 to 50 kcal/mole) 35 kcal. The heat of reaction of $\text{O}_2^\bullet\text{+e} \rightarrow \text{O}_2^{2-}$, is 110 kcal (Refs 1 & 4).

Most peroxides can be readily made by air oxidation of the-base compd or metal. They are characterized by the formation of hydrogen peroxide upon reaction with dil acid soln, the liberation of oxygen as a result of thermal decompn, and the liberation of oxygen upon reac-tion with w and other chem agents. The formation of hydrogen peroxide upon the hydrolysis of peroxides clearly indicates the relationship of these compds to hydrogen peroxide. For this reason, peroxides are thought of as being derived from hydrogen peroxide by replacement of one or both H atoms by organic, inorganic or organic/inorganic radicals (Ref 1). The decompn of $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ is readily accomplished (see Vol 7, H218-R to H222-L). The release of active (nascent- oxygen by this two-step mechanism in soln or the direct release of oxygen during thermal decompn, makes peroxides strong oxidizing agents, brisant expls, and extreme fire hazards when in contact with combustible materials, especially under high-temp conditions. The primary industrial uses of peroxides are as oxidizing agents and as initiators of polymerization. Mil uses are currently as liq propint constituents, ingredients in pyrots, and as polymerization initiators and curing agents (see below).

The prefix “peroxygen” is a general term referring to any peroxide linkage.
5) CondChemDict (1971), 671

Peroxides, Inorganic. The inorganic derivatives of hydrogen peroxide. These compds are described by a general formula, viz, E$^+_2\text{O}_2$, E$^{++}\text{O}_2$, etc; where “E” is an element. The metallic atoms are bonded to the oxygen bridge with ionic bonding. For convenience, differentiation is made between simple and complex inorganic peroxide compds. According to Vol'nov (Ref 5) simple peroxide compds also
include hydroperoxides. The hydroperoxides are characterized by the presence of the hydroperoxyl ion \( \text{HO}_2^- \) and are represented by the general formula \( \text{E-O-OH} \). In these compounds, inclusive of hydrogen peroxide, the peroxy-group is ionically bonded to the element and covalently bonded to the \( \text{H} \) atom. The ionic peroxides form well-crystallized hydrates and hydrogen peroxide adducts. There are some hydroperoxides that can be classified as peroxides and others as peroxycarboxylic acids. For example, \( \text{NaOOH} \) can be shown as a dimer, \( \text{Na}_2\text{O}_2\cdot\text{H}_2\text{O} \), whereas \( \text{NaOH}_3\text{Ti-O-OH} \) can be considered a peroxyacetic acid. Complex peroxide compounds include inorganic peroxides in which the peroxy-group is such (or in the form \( \text{H}_2\text{O}_2 \) and \( \text{HO}_2^- \)) as bonded to the element by a covalent bond rather than an ionic bond. Complex peroxide compounds also include the addition compounds formed with crystal \( \text{H}_2\text{O}_2 \). Again, according to Vol'nov, complex inorganic peroxide compounds can be divided into five groups:

1. Peroxyacids and their salts. In these compounds the peroxy-group is part of a complex anion. Within this category, one can distinguish between mononuclear and multinuclear peroxides and their salts. Generally, in these compounds the coordinating atoms are elements of the IV-VI group - nonmetals \( \text{C, N, P, S} \), or metals \( \text{Ti, V, Cr, Mo, W} \), etc. Peroxyacetato sulfuric acid

\[
\begin{array}{c}
\text{[O-O}=\text{O}]\text{H} \\
\text{[O-O}=\text{O}]\text{H}
\end{array}
\]

is an example of a mononuclear peroxyacid, and peroxydyesulfuric acid is an example of a multinuclear peroxyacid

\[
\begin{array}{c}
\text{[O-O}=\text{O}-\text{S]H} \\
\text{[O-O}=\text{O}-\text{S]H}
\end{array}
\]

The \( \text{O-O} \) bond length in a peroxy-group of peroxyacetic acid, for example in the \( \text{(NH}_4)_2\text{S}_2\text{O}_8 \) compd, is 1.46Å, which is less than the bond length in the \( \text{O}^2- \) ion (1.49Å).

2. Peroxide complexes which are neither peroxyacids nor their derivatives. These may also be divided into mononuclear and multinuclear compounds

The mononuclear peroxy complexes can further be divided into three subgroups: peroxycomplexes, perhydroperoxo complexes, and hydroperoxo complexes. The peroxycomplex subgroup includes compounds in which the peroxy-group is in the internal sphere, for example, \( \text{[UO}_2\text{O}_3^-} \cdot \text{O}_2\text{H}_2\text{O} \). The perhydroperoxo complexes contain hydrogen peroxide molecules in the internal sphere, for example \( \text{[Fe(H}_2\text{O)}_3\text{(H}_2\text{O)}])^3+ \), while the hydroperoxo complexes are characterized by the presence of the hydroperoxy radical \( \text{HO}_2^- \), for example, \( \text{K}_4[\text{UO}_2\text{O}_3\text{H}_2\text{O}] \).

Among the multinuclear peroxide complexes we may list:

\[\text{O}_2\text{Zr}[\text{O-O}-\text{ZrO}_2; \text{H}_4[\text{Cl}_5\text{Re-O-O-Cl}_5].2\text{H}_2\text{O} \]

and

\[\text{[NH}_3\text{CO-O-CO(NO}_3\text{H}_4]\text{NO}_3\]

In the last compound, the \( \text{O-O} \) bond length is 1.45 ± 0.06Å.

3. Peroxide hydrates. For example, \( \text{Na}_2\text{O}_2\cdot\text{H}_2\text{O} \)

4. Peroxyhydrates - molecular compounds. For example, \( \text{Na}_2\text{O}_2\cdot\text{H}_2\text{O} \) and \( \text{K}_2\text{CO}_3\cdot\text{H}_2\text{O} \). Peroxyhydrate compounds are closely related to the \( \text{KF-HF} \) type compounds. Ammonia and certain organic compounds having base properties also form molecular compounds containing \( \text{H}_2\text{O} \).

5. Peroxyhydroxy hydrates - molecular compounds containing crystal water and crystal hydrogen peroxide, for example, \( \text{BaO}_2\cdot\text{H}_2\text{O}_2\cdot\text{H}_2\text{O} \) and \( \text{Na}_2\text{SO}_4\cdot0.5\text{H}_2\text{O}_2\cdot\text{H}_2\text{O} \) (Ref 5).

History. The first known peroxide to be produced was \( \text{BaO}_2 \) as described by A. Humboldt in 1799. Later, C. Gay-Lussac and L. Thénard synthesized \( \text{Na} \) and \( \text{K} \) peroxides, and Thénard synthesized \( \text{H}_2\text{O}_2 \) in 1818 (Ref 17).

According to Vol'nov, the historical development of inorganic peroxide chemistry can be divided into four periods. The first period, from 1818 (Thénard's synthesis of \( \text{H}_2\text{O}_2 \)) to 1869 (the formulation of the Periodic Table by D.I. Mendeleev) is characterized by the wide-ranging investigations conducted by Thénard and his co-workers concerning the reaction of "oxidized water" which resulted in the development of a whole series of peroxide derivs as well as a more precise determination of the structure of \( \text{Na} \) peroxide.

The second period in the development of inorganic peroxide compounds can be considered to extend from the discovery of the Periodic Table to the application of physical chemistry
to the investigation of peroxide compounds at the beginning of this century. This period includes the classical studies of Melikov and Ptsarzhevskii, who uncovered a series of regularities in the formation of peroxyacids; the studies of R. de Forcrand in France dealing with the thermochemistry of inorganic peroxides; and the discovery of sodium perborates and carbonate peroxyhydrates of alkaline metals by Tanater. Also, during this period, a new type of peroxide compound was obtained for the first time (peroxyacids and their salts) by the use of electrochemical methods. M. Berthelot synthesized peroxydisulfuric acid, and E. Konstant and A. Henson produced potassium peroxydicarbonate. During this period, methods for industrial production of sodium peroxide and hydrogen peroxide were developed.

The third period is characterized by the extensive studies, both in the USSR and abroad, of the structure, properties, and bond characteristics of peroxide compounds. This period includes the work of Kazarnovskii and his co-workers concerning the structure of a series of peroxide compounds, his discovery of sodium superoxide, and the fundamental investigations carried out by the Canadian scientist Otto Maas and his co-workers concerning concentrated hydrogen peroxide.

"...Significant progress has been made in the Soviet Union in the post-war (or fourth) period in both the theoretical and applied fields. Kazarnovskii made important contributions to this progress as a result of his studies concerning the synthesis, properties, and reactivity of sodium superoxide and of the important new class of peroxide compounds—the inorganic ozonides. It is also appropriate to mention in this context the work of Brodskii, who was the first to establish the mechanism for the formation and disintegration of peroxide compounds via studies involving the use of the heavy oxygen isotopes. Also important was the work of A.M. Gurevich concerning the nature of uranium peroxide compounds, and the work of Kobozev on the synthesis of hydrogen peroxide by electrical discharge. Ship'tal'skii and his coworkers have made important studies of the catalytic decomposition of hydrogen peroxide. And at the Laboratory of Peroxide Compounds of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, Makarov has directed many important physico-chemical studies of peroxide compounds."

"...the chemistry of inorganic peroxide compounds is being developed mainly in universities and in private scientific research institutes in the United States, Great Britain, and West Germany. In the United States, for example, systematic studies of the properties of inorganic superoxides, especially the thermochemical properties of these compounds, have been carried out by Professor Kleinberg at the University of Kansas and Professor Margrave at Wisconsin University. Extensive investigations were conducted at the Massachusetts Institute of Technology, under the direction of Professor C. Satterfield, on the properties of concentrated hydrogen peroxide solutions."

"...At the Illinois Institute of Technology, Professor I.G. Solomon directed work on the synthesis of inorganic ozonides..."

"...In recent years, systematic X-ray studies of inorganic peroxides have been carried out by G. Föppl in West Germany and by N. Vannerberg and R. Shtomborg in Sweden..."

"...A series of conferences on peroxide compounds took place in the years from 1953 through 1961. A symposium on inorganic peroxides, superoxides, and peroxyhydrates was held in Philadelphia in 1953, and a symposium on peroxide reaction mechanisms was held at Brown University in 1960. In 1961, the British Society of Industrial Chemistry sponsored an international symposium on peroxide compounds. A general meeting dedicated to the chemistry of inorganic and organic peroxide compounds was held in Moscow at the end of 1961. The papers presented at the meeting showed that Soviet scientists have made significant contributions to this field of chemistry. However, the meeting also pointed out the areas of study which require a greater effort. Much more work must be done in the area of thermodynamics and kinetics. Also, a significant lag was noted in the field of analytical chemistry of peroxides and in X-ray structural investigations. To date, no really thorough investigations have been conducted, either by Soviet or foreign scientists, on the reactivity of inorganic peroxide compounds. It was established at that meeting that inorganic chemists working on
peroxides must concentrate their efforts on the synthesis of new superoxides and ozonides especially rich in oxygen. Such research should include the application of superhigh pressures of oxygen and ozone, concentrated solutions of hydrogen peroxide in nonaqueous solvents, and electrochemical methods. Physical chemists have an important role to play by determining the thermodynamic, kinetic, mechanistic, and structural properties of peroxide compounds...
(Ref 5)

Besides the ever-broadening scientific investigations which are being conducted world-wide in the field of inorganic peroxide compounds, it is also necessary to concentrate in the applied field on the sound development of continuous, safe, efficient and economical prodn methods so as to increase the utilization of inorganic peroxides.

Manufacture. In general, inorganic peroxides can be manufactured by one of the following methods: (1) by the action of hydrogen peroxide on oxides, hydroxides or salts (such as those of Ca, Sr, Zn, Mg), 2) by combustion of a metal or its lower oxide in air or oxygen (peroxidation), or 3) by electrolysis (anodic oxidation) of some salts. For instance, alkali peroxides and barium peroxide may be prepd by the 2nd method, while peroxides of Sr, Ca, Zn and Mg are prepd by the action of hydrogen peroxide with the oxide or hydroxide. Another variation of this method is pptn from a soln of a metallic salt with hydrogen peroxide in the presence of alkali.

The stability of inorganic peroxides increases as the cation is larger, which allows the spread of the negative charge over the extra oxygen atom. For instance, in the alkaline earth group, Ba, Sr, Ca, and Ba peroxide is the most stable and is the only one that can be prepd by direct peroxidation under atm press. Sr peroxide may also be prepd by peroxidation but, as it would require high pressure, it is preferable to prep it from Ca(OH₂) and hydrogen peroxide.

Uses. See below under specific compd. Generally, inorganic peroxides such as BaO₂ and SrO₂ are used in igniter compns for aircraft ejection app., percussion ignition compns, electric detonators, pyrots and gas prodn compns for automotive safety bags. Na₂O₂ is used in analytical chem., for example, to determine halogens in organic compds. The peroxides of Ca, Mg and Zn are used in medicine. ZnO₂ is employed where a slow evolution of O₂ is desired. Hydrogen peroxide has been used in propellant mixes, as, for example, the V-2 rocket of WWII. Inorganic peroxides have also been employed to supply O₂ for breathing purposes in closed spaces such as in submarines or mining operations.


Selected inorganic peroxides of military importance are presented below:

Barium Peroxide (Barium Dioxide, Barium Superoxide or Barium Binoxide). BaO₂, mw 169.36, white to grey tetragonal crystals or powd. mp 450° (Refs 15 & 33), bp 790–900° (decompn) (Refs 15, 17 & 33), d 4.96g/cc (Refs 15 & 33) & 5.43g/cc (Ref 17). V sol in cold w, sol in hot w (decompn), sol in dil acids (with decompn forming hydrogen peroxide), insol in acet. Lab prepn consists of heating loose BaO in CO₂-free O₂ at 500° (Refs 16 & 28). Other lab prepns are to be found in Refs 1, 3 & 6. A current industrial process reacts Ba(OH)₂ with 85% hydrogen peroxide vapors, forming the peroxide from a stoichiometric mixt within 20 mins. Most of the w is removed from the product at 55°, with the remaining traces taken off under
vacuum at 110–150°. The yield is 92.1% (Refs 20, 21 & 26)

BaO₂ is a strong oxidizing agent. Mixts with organic mats such as amines, alcohols or oils as well as with readily oxidizable mats such as P, Sb or charcoal are expld, and ignite easily by friction or on contact with a small amt of w (Refs 29, 30 & 31)

Kay (Ref 11b) has detd the purity of BaO₂ using a non-aqueous titrimetry technique. Nor-witz (Ref 16a) has reported techniques for the detn of impurities in BaO₂. In a subsequent report (Ref 32), he evolved a method for the detn of BaO₂ (or SnO₂) in small arms igniter compns. The technique consists of HCl soln of the peroxide, filt of insol mats, reaction of the

Table 1
Barium Peroxide
Chemical and Physical Requirements

<table>
<thead>
<tr>
<th>Requirements</th>
<th>Grade A</th>
<th></th>
<th>Grade B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1</td>
<td>Class 2</td>
<td></td>
</tr>
<tr>
<td>Moisture, max percent a</td>
<td></td>
<td></td>
<td>0.3</td>
</tr>
<tr>
<td>Apparent density, gm/ml min b</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>Available oxygen, min percent c</td>
<td>8.5</td>
<td>8.5</td>
<td>8.8</td>
</tr>
<tr>
<td>Total iron, max percent d</td>
<td></td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>Strontium, max percent e</td>
<td></td>
<td></td>
<td>0.85</td>
</tr>
<tr>
<td>Calcium, max percent f</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>Magnesium, max percent g</td>
<td></td>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>Sodium, max percent h</td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Aluminum, max percent i</td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Chlorides (as barium chloride), max percent j</td>
<td>see footnote 1</td>
<td>see footnote 1</td>
<td>0.1</td>
</tr>
<tr>
<td>Nitrate (as barium nitrate), max percent k</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insoluble matter, max percent m</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Grit, max percent n</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barium content, max percent o</td>
<td>76.0</td>
<td>76.0</td>
<td></td>
</tr>
</tbody>
</table>

Footnotes to Table 1
a – by wt loss after heating for 1.5 hrs at 275°
b – by weighing the content of a Scott volumeter cube
c – by K permanganate titration
d – by K permanganate titration after redn using a Jones reductor
e – gravimetrically as Sr sulfate
f – gravimetrically as Ca oxide
g – by bromate-bromide-thiosulfate titration
h – gravimetrically as MgNa uranyl acetate
i – after gravimetrically detg the combined oxides of Al and Fe, Al oxide is calcd by subtracting the percent Fe oxide found
j – by Ag nitrate-ammonium thiosulfate titration
k – by sulfuric acid titration after reaction with Devarda’s metal
l – to be specified by the interested agency using the Mil Spec
m – gravimetrically after dil HCl digestion and residue ignition
n – gravimetrically after dil HCl-conc nitric acid treatment and filt. The grit is then qual identified by the scratching sound it makes on a glass plate when rubbed with a steel spatula
o – gravimetrically as Ba sulfate;
(3) granulation requirements as shown in Table 2 below
sample soln with Ti soln and den of the TiO₂
formed spectrophotometrically at 410 nano-
meters. The procedures for detg BaO₂ and
impurities are shown in USAMilSpec, MIL-B-
153A, and are described briefly below
Toxicity. Highly toxic if swallowed. The LD₅₀
is 100mg/kg; max allowable air concn for an 8
hr day is 0.5mg/m³ (Refs 15 & 31).
The USA Mil Spec (Ref 25) contains the
following requirements for Grade A (anhyd with
some BaO and Ba₂O₃), Class 1 (> 45 microns,
nominal) and Class 2 (> 75 microns, nominal);
and Grade B (manufd by wet pptn method and
anhyd) BaO₂: (1) the color shall be grayish-
white or tan-white; (2) the chemical and physical
properties with requirements and criteria are
shown in Tables 1 & 2
Uses. BaO₂ is used in a number of igniter/
tracer/foze comps for mil ammo. An example
is that of a 40mm tracer compn, Mg₂BaO₃/Ca
resinate — 17.5/80.5/2.0% (Refs 4, 5, 7, 8, 9,
10, 11, 11a, 12, 13, 14 & 23). It imparts a green
color to burning pyrot compnts (Refs 4 & 15).
Doris and Cicone have reported the develop-
ment of an igniter compn for an aircraft ejection
app having the compn 100-325 mesh Mg (14.0),
BaO₂ (73.9), Zn stearate (0.9), chlorinated
rubber (5.3), Toluidine Red (0.9) and Ca resinate
binder (5.0%) (Ref 18). A GerP (Ref 7) was
obtained on low-pressure percussion ignition
comps, one of which has the following compn;
Cu (15), B (15), Ca₂Si (15), tetrazine (1.5) and
BaO₂ (53.5%). A FrP was reported (Ref 8) for
an electric safety detonator using Al powd/
BaO₂ — 20/80%. An interesting use for BaO₂
has been found in gas producing compns for
automotive safety. As reported by Hamasaki

<table>
<thead>
<tr>
<th>Grade A</th>
<th>Grade B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>Class 2</td>
</tr>
<tr>
<td>Thru No 100 US Standard sieve (150 microns)</td>
<td>99.9</td>
</tr>
<tr>
<td>Thru No 140 US Standard sieve, min (106 microns)</td>
<td>—</td>
</tr>
<tr>
<td>Thru No 170 US Standard sieve, min (90 microns)</td>
<td>98.0</td>
</tr>
<tr>
<td>Thru No 200 US Standard sieve, min (75 microns)</td>
<td>—</td>
</tr>
<tr>
<td>Thru No 325 US Standard sieve, min (45 microns)</td>
<td>90.0</td>
</tr>
</tbody>
</table>

Footnote to Table 2
a — gravimetrically, after shaking a sample thru the nest of graduated US Standard
b — Sieves shown in the Table

detg: Determination

et al (Ref 27) a compn comprised of a mixt of
BaO₂ (29.70), Zr (3.33), azodicarbonamide
(66.33) and SBR(?) (0.34%); or a similar mixt of
a metallic reducing agent, an inorg oxidizer,
and a gas former, is used to inflate within 30msec
after electrical ignition, a gas bag designed to
protect the occupants of an automobile upon
impact with an obstacle. Voi'nov (Ref 17)
lists other uses for BaO₂, such as in the polymeri-
ization of olefins and vinyl chloride; the oxidiz-
tion of ethylene to ethylene oxide; the prodn of
synthetic gas (CO-H₂) by partial oxidn of
hydrocarbons; the synthesis of hydrazine hydrate
from NH₄ and O₂; the decoloring of Pb and Te
glasses; as a starting subs for the prodn of met-
allic barium; and the use in analytical chem when
it is added to sulfuric acid to accelerate the com-
bustion of org substances

Refs: 1) Gmelin, Syst No 30 (1932), 92-104;
Ibid, Supplement (1960), 177 & 296–8
2) Mellor 3 (1922), 666-9
3) P. Askenas & R. Rose, ZAnorgChem 189, 1 (1930) & CA 24,
2839 (1930)
4) G.J. Schladt, “Stability Tests on Special Pyrotechnic Compositions”
PATR 42 (1931) 5) R.W. Scharf, “Investigation of
Hercules Non-Gaseous Powder For Use in 21
Second Time Fuze”, PATR 648 (1935)
6) J.D. Bernol et al, ZKristallogr 92, 344 (1935)
& CA 30, 2821 (1936) 7) J.D. Hopper,
“Study of Fundamental Properties of High
Explosives”, PATR 861 (1937)
8) D.R. Beeman, “Improved Functioning of M2 Tracer”, PATR
951 (1939) 9) H.J. Eppig, “Sensitivity of
Tracer Compositions Containing Barium Ni-	rate”, PATR 1254 (1943) 10) D. Hart,
“Compilation of Data On the Compositions of
Foreign Igniters and Tracers”, PATR 1335

Calcium Peroxide Octahydrate. CaO2.8H2O, mw 216.21, white powd or tetr cryst, mp 200° (–8H2O), bp 275° (exp), d 1.672g/cc. Sol in cold w, decomp by hot w; sol in acid, NH4 salts; insol in alc, eth and acet. Can be prep by reaction of an aq soln of a Ca salt such as CaCl2 with hydrogen peroxide (or sodium peroxide) with subsequent crysln. Readily converted to CaCO3 by CO2 (Ref 5). It is a strong oxidizing agent and reqs, according to ICC regulations, a yellow label. The octahydrate may be shipped in glass bottles, iron canisters or tins (Ref 8) Tests. Detd gravimetrically as the oxide after ignition (see under "Calcium ..." in USA Mil Spec requirements under Barium Peroxide) Toxicity. V low. However, when large amts of powd mat are being handled, a dust mask and gloves should be worn Uses. In baking dough, prod of hydrogen peroxide, vulcanization of rubbers, medicines, pharmacology, dentifrices, farming, chewing gums, etc. (Ref 6) Refs: 1) Gmelin, Syst No 28 (1956), 49 2) E.H. Riesenfeld & W. Nottebohm, ZAnorg-Chem 89, 405 (1914) & CA 9, 1436 (1914) 3) Mellor 3 (1922), 668 4) C. Nogareda, AnalesSocEspanolaFisicaQuim 28, 475 (1930) & CA 25, 2655 (1931) 5) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol 1, 2nd Edn, Academic Press, NY (1963), 937–8 6) I.I. Vol’nov, "Peroxides, Superoxides, and Ozonides of Alkali and Alkaline Earth Metals", Plenum Press, NY (1966), 62 &
Chromium Triaminotrioxide. See Vol 3, C302

Fluorine Peroxide. See Vol 6, F135-R

Hydrogen Peroxide. See Vol 7, H218-R to H222-L

Lead Peroxide. See Vol 7, L9

Manganese Peroxide. See in this Vol under Manganese Dioxide

Potassium Peroxide. $K_2O_2$, mw 110.20, white (to yel) amorph and delq mass, rhomb cryst; mp 490° (decomp), d 2.40g/cc, decompd by w or alc with evoln of $O_2$. It can be produced by heating $K_2O$ in a vacuum (10° mm) at temps above 450°. K peroxide is readily oxidized to $KO_2$ in air (Refs 1 & 4). It is a powerful oxidizing agent which is shipped under yellow label. The reaction of the peroxide in large amts wth $w$ is explos at RT. Spont ign also occurs with metallic powds such Al in the presence of small amts of $w$, on contact with $Ac_2O$, by shaking with KOH or NaOH solns and by percn with org mats such as hay, bark, S, cotton, etc (Refs 5, 7 & 8). Tests. The K content can be quant detd by flame emission spectroscopy (Ref 4a), while the oxygen content can be quant detd by gasometric analysis (see Vol 6, G15-R thru G16-R) or by FeSO$_4$–KmO$_4$ titrimetry (Ref 3a). Toxicity. Poisonous if ingested. An irritant to skin and eyes (Ref 8).

Uses. Potassium peroxide is used as an oxidizing agent and in oxygen generating units for gas masks (Ref 5). Another use has been found by Hatterer who developed a device which extracts the thermal energy from nuclear reactors in a reaction which generates $H_2$ and $O_2$ gases by the dissociation of $w$; viz, (1) $K_2O_2 + H_2O \rightarrow 2KOH + \frac{1}{2}O_2$; (2) $2KOH + 2K \rightarrow 2K_2O + H_2$; and (3) $2K_2O + heat \rightarrow K_3O_3 + 2K$. This cyclic and self-contained process lowers thermal pollution and provides the gases as valuable by-products (Ref 6).


Sodium Peroxide (Sodium Dioxide, Superoxide or Solozone). $Na_2O_2$, mw 77.98, yel-white powd, hex cryst; mp 460° (decomp, Ref 15), 540° (decomp, Ref 10); bp 657° (decomp, Ref 15), 636° (decomp, Ref 10); d 2.805g/cc (Ref 15), 2.47g/cc (Ref 9b) or 2.60–2.62g/cc (Ref 10). Reacts with $w$ to form NaOH and hydrogen peroxide plus a large amt of heat ($Q_{soln} +34 \times 0.3$kcal/mole). It is decompd by hot $w$, alc and $NH_4$; soln in dil acid and insol in alk. Lab prepn of $Na_2O_2$ involves air oxidn of Na to $Na_2O$. The $Na_2O$ is then oxidized completely to $Na_2O_2$ in $O_2$ at 200–350° (Refs 1, 4, 5 & 11). There are several coml proc for the manuf of $Na_2O_2$, one of which uses Na which is heated either in Al trays or on a rotating cylindrical drum, and then oxidized by a current of dry air (CO$_2$-free) (Refs 6a, 13 & 14). In another procedure, hydrazobenzene is oxidized in the presence of Na alcoholate to produce $Na_2O_2$ and regenerated ethanol plus azobenzene (Ref 10).

Sodium peroxide is a very powerful oxidizing agent. It can be caused to detonate when mixed, in the presence of $w$, with reducing agents such as $SbCl_3$, $As_2O_3$, $SbCl_5$, $Al(CNS)_3$. 

9) ChemRubHndbk (1975), B-78

9) CondChemDict (1973), 158
powd Fe, Al and CaC, as well as finely dispersed S, AlCl₃, ethanol, ether, glycerine and sugar (Refs 6 thru 10 & 16). Explns upon intimate mixt at RT have occurred with mats such as acet ac (Refs 3 & 16), Ca acetylide (Ref 6), PCl₃ (Ref 2), MnO₂ (Ref 16); Carbon or P (Refs 3, 6 & 16) and water (Refs 1a, 3a & 7). Also, friction has caused the expn of an NH₄ peroxodisulfate/N₂O₅ mixt (Ref 8). Spont Ign has occurred upon mixt or contact of N₂O₅ at RT with mats such as moist cloth, paper or wood (Refs 3 & 16); H₂S or various peroxides (Ref 8); CO₂ or metallic Na (Refs 6 & 9); nonmetal halides (Refs 8 & 9); org lqts (benz, eth, aniline, etc) and w (Ref 3); and AgCl and charcoal (Ref 7). Percussion has caused spont ign of mixts of various org mats with NaOH or KOH and N₂O₅ (Ref 17). Percussion has also caused spont ign to occur when N₂O₅ is mixed with mats such as hay, bark, cotton or powd S (Ref 17). When Na and N₂O₅ were heated together to the mp of Na (97.5°) under Ar, expln has also occurred (Ref 15).

Tests. The compd can be quant detd by flame emission spectroscopy (Ref 14a) and by FeSO₄-KMnO₄ titrmtr for “active” N₂O₅ (Ref 9b). Toxicity. Poisonous if ingested. Highly irritating to skin and mucous membranes (Ref 17).

Uses. N₂O₅ is prod in tonnage qunts by many countries. Currently, the USA produces over 8000 tons/yr (Ref 10). It can be used in oxidizing fusions of metals (Ref 11). However, its primary use is as an oxidizing or bleaching agent (Refs 13 & 14). Another use, of mil interest, is for O₂ generation and purification sys for submarines and space vessels (Ref 14).


Strotrurn Peroxide (Strontium Dioxide). SrO₂, mw 119.63; white powd, tetrag cryst; mp 215° (decompn; Ref 14), 357-410° (decompn; Ref 6), 410-450° (decompn; Ref 7); d 4.56g/cc. Sr sl in cold w, decompd by hot w, v sl in alc and NH₄Cl soln; insol in acet. Lab prepn frm hydroxide and carbonate-free SrO under an O₂ press of 200-50 atm at 350-400° (Refs 1, 3, 7 & 8). Compl prepn consists of reacting a SrOH₂O soln with a dil soln of hydrogen peroxide (Refs 3, 7 & 8). To produce material dense enough for pyrot usage (2.0-2.1g/cc), the commercial reaction medium is maintained at 50-75°. The final prod is moistened with hot concd Sr(NO₃)₂ soln and dried at 120-200° (Ref 4).

Strotrum peroxide is considered a dangerous oxidizing material which will readily ignite.
explosively when mixed with combustible substances. By itself, heat, shock or catalysts may cause violent decompn of SrO₂. Contact with w produces heat (Refs 6, 9 & 10)

Tests. SrO₂ is detd in the pure state by non-aqueous titrimetry (Ref 5), and in igniter mixes spectrophotometrically at 410 nanometers by reaction with Ti(IV) soln (Ref 13)

Toxicity. Injurious to skin or mucous membranes (Ref 6)

Table 3
Strontium Peroxide
Chemical and Physical Requirements

<table>
<thead>
<tr>
<th>Requirements</th>
<th>Grade B</th>
<th>Grade C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available O₂, min, % a</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>Moisture, max, % b</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Hygroscopicity, max, % c</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Apparent density, min, gm/ml d</td>
<td>1.30-2.00</td>
<td>0.85</td>
</tr>
<tr>
<td>Barium, max, % e</td>
<td>0.1</td>
<td>0.45</td>
</tr>
<tr>
<td>Calcium, max, % f</td>
<td>0.3</td>
<td>0.15</td>
</tr>
<tr>
<td>Magnesium, max, % g</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Sodium, max, % h</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron, max, % i</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>Aluminum, max, % j</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Nitrate, calcd as Sr(NO₃)₂, max, % k</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Chloride, calcd as SrCl₂, max, % l</td>
<td>0.1</td>
<td>0.10</td>
</tr>
<tr>
<td>Total impurities other than SrO, max,%</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Footnotes to Table 3:
a—by K permanganate titration
b—gravimetrically by loss in wt after heating
c—gravimetrically by exposure of a sample to 75% RH
d—by weighing the content of a 50ml graduated cylinder
e—spectrophotometrically by atomic absorption
f—spectrophotometrically by atomic absorption
g—spectrophotometrically by atomic absorption
h—spectrophotometrically by atomic absorption
i—spectrophotometrically at 500 nanometers using ortho-phenanthrolin-hydroxylamine acetate solns as colorimeteric reagents
j—gravimetrically as the oxide
k—by sulfuric acid titration subsequent to a Devarda redn
l—by Ag nitrate—NH₄ thiocyanate titration

The USA Mil Spec (Ref 12) has the following requirements for Grade B SrO₂ (mfd by a wet pptn method, consisting essentially of anhyd SrO₂), and Grade C SrO₂ (mfd by a wet pptn method, consisting essentially of anhyd SrO₂ with a definite hygroscopicity requirement to control the stability of the mat): (1) The material shall be a free flowing white powd; (2) The chemical and physical properties with requirements and criteria are shown in Table 3 (3) Granulation requirements as shown in Table 4 below:

Table 4
Particle Size Distribution a

<table>
<thead>
<tr>
<th></th>
<th>Grade B</th>
<th>Grade C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thru No 80 (180 microns)</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>Thru No 100, min</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>(150 microns)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thru No 140, min</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>(106 microns)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnote to Table 4:
a—gravimetrically after shaking a sample thru the nest of graduated US Standard Sieves shown in the Table

(4) The SrO₂ shall be free of grit, dirt, foreign matter or other injurious material Uses. SrO₂ is used as an oxidizer to impart a red color to pyrots, and as a means of reducing projectile base drag (Refs 6 & 11). It is also employed in a variety of igniter comps for pyrot tracers (Ref 5a)

Earth Metals", Plenum Press, NY (1966), 64-6
8) Kirk & Othmer 14 (1967), 750-1
9) Merck (1968), 988   10) CondChemDict (1971), 830
11) W.J. Richard, "Use of Pyrotechnics to Reduce Base Drag", ProcSymp
13) G. Norwitz & M. Galan, "Determination of Barium and Strontium Peroxides (Active Oxygen) in Igniters in Small Arms
Tracer Ammunition", FA-TT-75069 (1975)
14) ChemRubHdbk (1975), B-143 & F-147

The following Table contains a listing of explosive inorganic peroxides which are not currently used as expl ordn material.
## Table 5

### EXPLOSIVE NATURE OF INORGANIC PEROXIDES

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Remarks Concerning Explosiveness</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystalline Hydrogen Peroxides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Borate</td>
<td>May react violently in close contact (grinding or heating) with oxidizable materials</td>
<td>Kirk &amp; Othmer 11</td>
</tr>
<tr>
<td>Hydrogen Peroxide, BN₃O₄·H₂O</td>
<td></td>
<td>(1966), 395</td>
</tr>
<tr>
<td>Sodium Pyrophosphate Hydrogen Peroxide, Na₆O₇P₂·2H₂O₂</td>
<td></td>
<td>Ibid</td>
</tr>
<tr>
<td>Triethylamine Hydrogen Peroxide, C₆H₁₅N·4H₂O₂</td>
<td>Ibid</td>
<td>Ibid</td>
</tr>
<tr>
<td><strong>Metal Peroxides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury Peroxide, HgO₂</td>
<td>Explodes on impact or friction when mixed with H₂O₂</td>
<td>Mellor 4</td>
</tr>
<tr>
<td>Zinc Peroxide, ZnO₂</td>
<td>The hydrated peroxide (of indefinite compn), explodes at 212°, and mixes with Al or Zn powders burn brilliantly</td>
<td>Mellor 4 (1940), 530 &amp; Sidgwick, ChemElem 1 (1950), 270</td>
</tr>
<tr>
<td><strong>Metal Peroxomolybdates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Tetraperoxomolybdate (2'), MoNa₂O₈</td>
<td>Explosive decomp in under vacuum</td>
<td>H.M. Castrantes et al, &quot;Fire and Explosion Hazards of Peroxy Compounds&quot;, ASTM Special Publ No 394, Phila (1965), 5</td>
</tr>
<tr>
<td><strong>Peroxides in Solvents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peroxomonosulfuric Acid, H₂O₅S: Solvent</td>
<td>Exploses violently on warming above 0° or on contact with w. acet, alcohols or aromatic compds</td>
<td>1) A. Bayer, Ber 33 (1900), 858 2) G. Toennies, JACS 59 (1937), 552 3) Sidgwick, ChemElem 1 (1950), 939 4) J.O. Edwards, C&amp;EN 33 (1955), 3336</td>
</tr>
</tbody>
</table>

(continued)
Table 5 (continuation)
Explosive Nature of Inorganic Peroxides

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Remarks Concerning Explosiveness</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxodisulfuric Acid, H₂O₆S₂</td>
<td>Explodes on uncontrolled contact with aniline, benz, ethanol, eth, nitrobenz or phenol</td>
<td>J. D'Ans et al, Ber 43, 1910 (1911); Ibid, ZAnorgChem 73, 1911 (1911)</td>
</tr>
<tr>
<td>Peroxomonophosphoric Acid, H₃O₅P</td>
<td>Ignition when an 80% soln contacts org material</td>
<td>H.M. Castrantas et al, “Fire and Explosion Hazards of Peroxy Compounds”, ASTM Special Publ No 394, Phila (1965), 5</td>
</tr>
<tr>
<td>Peroxomonosulfuric Acid, H₃O₅S</td>
<td>Explodes above 0° on w contact and by expl decompn in large amts</td>
<td>J.O. Edwards, C&amp;EN 33, 3336 (1955); also see Vol 2, C69-L &amp; R</td>
</tr>
<tr>
<td>Peroxononitrile Acid, HNO₄</td>
<td>Pure material decomposes explosively at -30°. Solns in w or acet ac over 70% HNO₄ decompose autocatalytically to expln</td>
<td>R. Schwarz, ZAnorgChem 256, 3 (1948)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peroxoacid Salts</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CrH₆N₂O₁₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium Peroxoborate, BH₄NO₃</td>
<td>Explosive decompn under vacuum</td>
<td>H. Menzel et al, OesterChemZtg, 28, 162 (1925)</td>
</tr>
<tr>
<td></td>
<td>Explodes violently on addition of Ag salts</td>
<td>Mellor 10 (1947), 466</td>
</tr>
<tr>
<td>Ammonium Tetraperoxochromate (3⁺),</td>
<td>Explodes at 50°, on impact, or in contact with sulfuric acid</td>
<td>Mellor 11 (1943), 356</td>
</tr>
<tr>
<td>CrH₁₂N₂O₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium Peroxochromate (3⁺), Ca₃C₆₂O₁₂</td>
<td>Explodes at 100°</td>
<td>J.H. Raynolds et al, JACS 52 (1930), 1851</td>
</tr>
</tbody>
</table>

(continued)
Table 5 (continuation)
Explosive Nature of Inorganic Peroxides

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Remarks Concerning Explosiveness</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Diperoxoo-</td>
<td>Explodes on heating</td>
<td>Mellor 9 (1939), 795</td>
</tr>
<tr>
<td>orthovanadate (2⁻), K₂O₆V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium Pentaperoxoo-</td>
<td>Explodes above 0°</td>
<td>Meller 11 (1943), 357 &amp;</td>
</tr>
<tr>
<td>dichromate (2⁻), Cr₂K₂O₁₂</td>
<td></td>
<td>Sidgwick, Chem.Elem. 1 (1950), 1007</td>
</tr>
<tr>
<td>Potassium Peroxoferate (2⁻),</td>
<td>Explodes on heating, impact, or in contact with charcoal, P, S or sulfuric acid</td>
<td>D.K. Goralevich, J.RussPhChem-</td>
</tr>
<tr>
<td>FeK₂O₅</td>
<td></td>
<td>Soc 58, 1155 (1926)</td>
</tr>
<tr>
<td>Potassium Peroxomonosulfate,</td>
<td>Forms explosive mixtures with as little as 1% of organic matter; dangerously unstable</td>
<td>H.M. Castrantas et al,</td>
</tr>
<tr>
<td>HKO₅S</td>
<td></td>
<td>“Fire and Explosion Hazards of Peroxy Compounds”, ASTM Publ No 394, Phila (1965), 5</td>
</tr>
<tr>
<td>Potassium Tetraperoxochromate (3⁻),</td>
<td>Explodes at 178° or in contact with sulfuric acid; the impure salt is explosive</td>
<td>Meller 11 (1943), 356</td>
</tr>
<tr>
<td>CrK₃O₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium Tetraperoxomolybdate (2⁻),</td>
<td>It is an explosive</td>
<td>K.F. Jahr, FIAT Rev of Ger Sci: InorgChem, Part III (1948), 170</td>
</tr>
<tr>
<td>K₂MoO₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium Tetraperoxotungstate (2⁻),</td>
<td>Explodes on rapid heating to 80° or by friction</td>
<td>Meller 11 (1943), 836</td>
</tr>
<tr>
<td>K₂O₆W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver Peroxochromate, AgCrO₅</td>
<td>Reacts explosively with 50% sulfuric acid upon being warmed from −80° to −30°</td>
<td>E.H. Riesenfeld et al, Ber 47, 548 (1914)</td>
</tr>
<tr>
<td>Sodium Peroxoborate, BH₄NO₂</td>
<td>Detonates upon light friction</td>
<td>Anon, AngChem 65, 41 (1963)</td>
</tr>
<tr>
<td>Sodium Tetraperoxochromate (3⁻), CrNa₃O₅</td>
<td>Explodes at 115°</td>
<td>Meller 11 (1943), 356</td>
</tr>
<tr>
<td>Sodium Tetraperoxomolybdate (2⁻), MoNa₂O₈</td>
<td>Explosive decomp under vacuum</td>
<td>H.M. Castrantas et al, “Fire and Explosion Hazards of Peroxy Compounds”, ASTM Publ No 394, Phila (1965), 5</td>
</tr>
<tr>
<td>Sodium Tetraperoxotungstate (2⁻), Na₃O₆W₂</td>
<td>Explodes feebly on warming</td>
<td>Meller 11 (1943), 835</td>
</tr>
<tr>
<td>Tetramin zinc Peroxodisulfate, H₂N₄O₄S₂Zn</td>
<td>Explodes on heating or impact</td>
<td>G.A. Barbieri et al, ZAnorgChem 71, 347 (1911)</td>
</tr>
<tr>
<td>Tetramethylammoniumpentaperoxodichromate (2⁻),</td>
<td>Explodes on contact with sulfuric acid or on moderate heating</td>
<td>Meller 11 (1943), 358</td>
</tr>
<tr>
<td><a href="NH%E2%82%83">Cr(O₈)₆Cr(O₂)₂</a>₂(C₆H₁₄)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued)
Table 5 (continuation)

Explosive Nature of Inorganic Peroxides

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Remarks Concerning Explosiveness</th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Peroxoammine Chromium Complexes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Dianinoethaneammine-diperoxochromium (IV), [Cr(C(_2)H(_9)N(_2) \times \text{(NH})(_3)(O(_2))_2)_2 \times H(_2)O]</td>
<td>The monohydrate explodes or decomps at 115° during slow or moderate heating. It is potentially explosive at 25°</td>
<td>D.A. House et al, InorgChem 6, 1077 (1967)</td>
</tr>
<tr>
<td>1,2-Dianinoethaneaquadi- perxochromium (IV), [Cr(C(_2)H(_8)N(_2))_2(O(_2))_2 \times H(_2)O]</td>
<td>Explodes at 96—7° when heated at 2°/min and is light sensitive</td>
<td>D.A. House et al, InorgChem 5, 840 (1966); R.F. Childers et al, InorgChem 7, 749 (1968)</td>
</tr>
<tr>
<td>1,2-Dianino-2-Methylpropane- aquadiperxochromium (IV), [Cr(C(_4)H(_7)N(_3))_2(O(_2))_2 \times H(_2)O]</td>
<td>Explodes at 83—4° when heated at 2°/min. It is potentially explosive at 20—5°. Caution is reqd in prepn</td>
<td>D.A. House et al, InorgChem 6, 1078 (1967)</td>
</tr>
<tr>
<td>1,2-Dianino-2-methylpropane- oxiderochromium (VI), Cr(C(_4)H(_7)N(_3))(O(_2))_2(O)</td>
<td>A very explosive black ppt formed during the prepn of 1,2-dianino-2-methylpropanaquaquadiperoxidium (IV) monohydrate. Caution in isolation must be used</td>
<td>D.A. House et al, InorgChem 6, 1078, footnote 6 (1967)</td>
</tr>
<tr>
<td>1,2-Dianinopropane-aquaquadiperoxidium (IV), [Cr(C(_3)H(_10)N(_2))_2(O(_2))_2 \times H(_2)O]</td>
<td>The dihydrate explodes spontaneously at 20—5° and at 88—90° during slow heating</td>
<td>D.A. House et al, InorgChem 5, 840 (1966)</td>
</tr>
<tr>
<td>Dianilineoxodiperoxo- chromium (VI), Cr(C(_1)H(_4)N(_2))(O(_2))_2(O)</td>
<td>Very explosive when dry. Prepn and sepns of the compd has injured several scientists</td>
<td>D.M. Adams et al, JChemEduc 43, 94 (1966)</td>
</tr>
<tr>
<td>Diethylenetriaminodiperoxo- chromium (IV), [Cr(C(_4)H(_7)N(_3))(O(_2))_2 \times H(_2)O]</td>
<td>Explodes at 109—10° when heated at 2°/min</td>
<td>D.A. House et al, InorgChem 5, 840 (1966)</td>
</tr>
<tr>
<td>Dimethyl etheroxodiperoxidio- chromium (VI), Cr(O(_2))_2(O).O(CH(_3))_2</td>
<td>The bl solid explodes with extreme brisance at —30°</td>
<td>R. Schwarz &amp; G. Elstner, Ber 69, 575—9 (1936)</td>
</tr>
<tr>
<td>Hexamethylenetetrammonium tetraperoxochromate (V)?, [Cr(C(_5)H(_6)(N(_2))_2(Cr(O(_2))_4)_4</td>
<td>Dry material explodes in prepn</td>
<td>D.A. House et al, InorgChem 6, 1078 (1966)</td>
</tr>
<tr>
<td>Oxodiperoxodi peridine- chromium (VI), Cr(C(_1)H(_2)N(_2))(O(_2))_2(O)</td>
<td>Very explosive when dry, a very powerful oxidant, destroy surplus after use with dil alk</td>
<td>D.M. Adams et al, JChemEduc 43, 94 (1966); S. Caldwell et al, InorgChem 8, 151—5 (1969); J.C. Collins et al, OrgSynth 52, 5—8 (1972)</td>
</tr>
<tr>
<td>Oxodiperoxopyridine- chromium (VI), Cr(C(_5)H(_5)N(_2))(O(_2))_2(O)</td>
<td>A powerful and selective oxidant which is a very brisant explosive when dry. Destroy surplus after use with alk</td>
<td>Ibid</td>
</tr>
<tr>
<td>Triaminediperoxochro- mium (IV), Cr(N(_3))_3(O(_2))_2</td>
<td>Caution in handling reqd! Sudden shock or rapid heating will cause explosion or incandescence. Heating at 20°/min will cause a very brisant explosion at 120°</td>
<td>G.B. Kaufman, InorgSynth 8, 133 (1966); R.G. Hughes et al, InorgChem 7, 882 (1968)</td>
</tr>
</tbody>
</table>
Peroxides, Organic. These are compounds containing carbon with at least two oxygen atoms linked together in the same manner as the oxygen atoms in molecular oxygen: i.e., \( \text{O}-\text{O} \) (see Fig 1 under Inorganic Peroxides above). This type of linkage exists because oxygen is the primary source of the \(-\text{O}-\text{O}-\) linkage in organic peroxides. Indeed, this linkage is the result in all types of organic peroxide prep, whether by direct air oxidation or by reactions of organic compounds with peroxodic materials derived from oxygen such as \( \text{H}_2\text{O}_2 \), alkali metal peroxides, or ozone. Organic peroxide compounds are more prone to combustion and explosion than their inorganic analogues because of the presence of built-in organic fuel. The difference in free energy between a peroxo compound and its decomposition products is often greater in the case of organic compounds than inorganic (Refs 4, 12, 14a & 20). Various types of explosive tests have been developed for peroxides which will be presented below under "Safety" and in the treatments of individual peroxide compounds when available (Refs 4, 12, 14a, 18, 20, 22 & 26).

Table 6 presents a structural definition of each class of organic peroxide, the chemical reactions of each class and the comparative explosiveness of each class (Refs 4, 12, 14a, 20 & 21). Also, see under Organic Hydroperoxides in Vol 7, H224-R to H227-R and under Ozonides in this Vol.

History. According to Kirk and Othmer (Ref 14a), the first synthesis of an organic peroxide was the prep of benzoyl peroxide reported by B.C. Brodie in 1859. Since then many types of organic peroxides have been synthesized and isolated. Industrial interest in the use of organic peroxides began in the early 1900's when it was found that benzoyl peroxide was an effective bleaching agent for edible oils, and somewhat later, an excellent bleaching agent for flour. With the demand for synthetic rubber and plastics during WWII, the use of organic peroxides as initiators of polymerization began to develop. The continued growth of free radical polymerization after the war stimulated the development of many organic peroxide products to meet a variety of needs. Today, organic peroxides are used as initiators in the manufacture of the major polymers such as polyethylene, poly(vinyl chloride), polystyrene, poly-ester thermosets, polycrylates, styrene-butadiene rubber and many others; as crosslinking agents for polyethylene, ethylene-propylene copolymers and silicone rubber; as bleaching agents for flour; and, in the case of peroxyacids, as epoxidizing agents. There are about forty to fifty different organic peroxides commercially available in a total of approximately seventy organic peroxide products.

About 8,000 metric tons of peroxides were consumed in 1972. This consumption was strongly stimulated by the rapid growth in reinforced plastics (Ref 23). The largest volume product is benzoyl peroxide which is used in polystyrene and polyester markets for such items as toys, automobiles, furniture, marine, transportation and mil requirements. Also, methyl ethyl ketone peroxide is used in large volumes to cure (as a catalyst) styrene-unsaturated polyester adhesive resins used in mil ammo adhesive applications, as well as in glass fiber reinforced plastic products such as boats, shower stalls, tub components, automobile bodies, sports equipment, etc. The monomers are growing slowly because of some substitution of the peroxydicarbonates and azo compounds (Refs 8, 9 & 23).

Again, according to Kirk and Othmer (Ref 14a), the systematic study of the chemistry of organic peroxides began in the 1930's. In recent years the amount of research in the field has increased considerably, and not only have many new organic peroxides been isolated but many of the peroxide reaction mechanisms have been elucidated. The development of safer, easily handled and more efficient polymerization initiators is a major goal.

With reference to the mil literature available for unlimited publication, acetone peroxide has been considered for use as a detonating expl (Ref 1a), but was found to be too volatile at RT for such an application (see Vol 1, A42-R to A45-R).
<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Reactions</th>
<th>Explosiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydroperoxides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary, secondary, or tertiary alkyl hydroperoxides; ( R-O-O-H )</td>
<td>Liq or crys; w sol; stronger acids than the corresponding alcs; react readily to form other org peroxides; heterolytic, homolytic and metallic oxidn-redn cleavage of the (-O-O-) bond can occur; easily reduced, re-arranged and decomp; used in org synthesis as oxidizing or hydroxylating reagents</td>
<td>Lower members prone to explosion; brisance decreases with increasing chain length and lower ( \text{O}_2 ) activity; explode at temps over 80°</td>
</tr>
<tr>
<td>Organomineral hydroperoxides; ( R_m^m(OH)_n ) (( m=\text{metal or metalloid} ))</td>
<td>Behave as covalent org compds; undergo homolytic thermal decompn or photo-decompn; most compds are v thermally stable; hydrolyzed v readily; form alkyl hydroperoxides with anhyd HCl</td>
<td>Insensitive to friction and impact; explode on rapid heating</td>
</tr>
</tbody>
</table>

**\( \alpha \)-Oxy- and \( \alpha \)-Peroxy-Hydroperoxides and Peroxides**

| General structure; viz, \( C-O-O- \) | Hydrolyze with w to form dihydroxyperoxides or polymers; can be reduced, oxidized or dehydrated to expi polymers (\( RCH-O-O- \)) with \( \text{P}_2\text{O}_5 \); react with aldehydes to form symmetrical prods | Decomp on heating; lowest member expl; others moderately stable |
| **\( \alpha \)-Oxyhydroperoxides (1),** \( C-O-OH \) | | |
| **\( \text{Gem-dihydroperoxide (2),}** \( C-O-OH \) \( C-O-OH \) | W sol and decomp slowly with evoln of \( \text{O}_2 \) and formation of expi polymeric peroxides; can be reduced and hydrolyzed; thermal decompn leads to progressive bond cleavage of \(-O-O-\), \( C-O-\) and then \( C-C \) bonds | Polymeric peroxides formed as a decompn product are extremely expl |
| \( \alpha,\alpha' \)-Dioxyperoxides (3), \( -C-O-O-C- \) | Easily reduced; decompn to dibasic acids by ferrous salts; thermal decompn yields aldehydes, ketones, carboxylic acids and alcohols; dehydrated to ozonides and other cyclic peroxides | Lowest member, \( \text{HOCH}_2-O- \text{O-CH}_2\text{OH} \), is a dangerously expli solid; the next higher members are liqs, and the longer chain members are solids of decreasing explosiveness |

(continued)
### Table 6 (continuation)
Comparison of the Properties of Organic Peroxides

<table>
<thead>
<tr>
<th>Structure Description</th>
<th>Chemical Reactions</th>
<th>Explosiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Oxy-α'-hydroperoxy-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>peroxides (4)</td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H⁺ → C=O</td>
<td>Very slight expl qualities</td>
</tr>
<tr>
<td></td>
<td>RC(O)Cl → C(-O-O-C-R)₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Test-Phosphines → C-O-O-C-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dehydrating Agents → OH OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb(-O-C₆H₄)₄ → C=O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CuSO₄ →</td>
<td></td>
</tr>
<tr>
<td>α,α'-Dihydroperoxy-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>peroxides (5)</td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>RC(O)Cl → C-O-O-C-</td>
<td>Very slight expl qualities</td>
</tr>
<tr>
<td></td>
<td>O-O-CR O-O-CR</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td>Cyclic gem-diperoxides (6)</td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Not readily hydrolyzed; can be reduced by Zn and acet ac or Grignard reagents; thermal decompn yields original ketone, etc</td>
<td>Very expl lower members; aralkylidene members are stable to mp's (180–225°)</td>
</tr>
<tr>
<td>Cyclic-gem-triperoxides (7)</td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Basic hydrolysis yields carboxylic acids as decompn prods</td>
<td>Same as above</td>
</tr>
<tr>
<td>Polymeric α-Oxy- and</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Peroxyperoxides (8),</td>
<td><img src="image" alt="Chemical Diagram" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Viscous liqs or amorph solids; difficult to characterize; low mw members can be sept by chromatography</td>
<td>Dangerously expl!</td>
</tr>
<tr>
<td>α-Hydroperoxides (9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Higher homologs tend to hydrolyze to original aldehyde; redn to carbonyl and hydroxy comps; ferrous salts catalyze decompn to free radicals; thermal decompn involves homolytic and heterolytic processes</td>
<td>Lowest member, hydroxydimethyl peroxide is an unstable expl; other members are less expl than corresponding dialkyl peroxydes and are reasonably stable to storage and vacuum distn</td>
</tr>
</tbody>
</table>

(continued)
### Table 6 (continuation)
**Comparison of the Properties of Organic Peroxides**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Reactions</th>
<th>Explosiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>α-Oxy- and α-Peroxyl-Hydroperoxides and Peroxides (continuation)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gem-peroxides (10),</strong> C—O—O—R</td>
<td>Colorless soln in org solvents, w insol; readily acid hydrolyze to starting reactants; redn to alcohols with H₂ and Raney Ni</td>
<td>Lower numbers are shock-sensitive and explode on spark contact; explosiveness solvent moderated</td>
</tr>
<tr>
<td><strong>Ozonides (11),</strong> C—O—O</td>
<td>Acid and base hydrolysis to yield all possible org compds; redn by LiAlH yields carbonyl and hydroxyl-contg derivs; thermal decompn prods are all possible org compds</td>
<td>Highly expl; decompd by ferrous salts, Ag, Pd and Pt; stable in storage; distillable under vacuum</td>
</tr>
<tr>
<td><strong>α-Hydroxyalkyl peroxycarboxylates (12),</strong></td>
<td>No information</td>
<td>No information</td>
</tr>
<tr>
<td>O—C—O—O—C—R</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Peroxides

| **Dialkyl peroxides (1), R—O—O—R’** (R and R’ are = or ≠ primary, secondary, tertiary alkyl, cycloalkyl, aralkyl and heterocyclic radicals) | Homolytic decompn when heated or irradiated with prod of free radicals for org synthesis; difficult to hydrolyze and reduce; rearrangement crosslinking and polymerization; polymeric peroxides are thick liqs or amorph whisk powds; used as polymerization catalysts | Primary radicals are unstable, lowest members such as dimet peroxide are shock sens and dangerous expls; sensitivity lessens with increasing mw; polymeric peroxides (copolymer of olefins and O₂) explode on heating |
|                                                                                                                               | Act as covalent org compds; v thermally stable; homolytic thermal and photo decompd; hydrolyze v readily, hence v useful in org synthesis | Insens to friction and impact; violent decompn on rapid heating |
| **Organoinmineral peroxides (2), RₘM—O—O—Rₙ** and RₙM—O—O—Rₙ |                                                                                                               |                                                                               |

### Peroxy Acids (Peracids)

| **Peroxy carboxylic Acids (1), RC(O₂H)ₙ** (R=alkyl, cycloalkyl, aryl, or heterocyclic; n=1 or 2) | Acid or base hydrolysis with rate decreasing with mw increase; dil NaOH decomposes acids yielding O₂; dimeric as solids; H-bonded in soln; pure liq and vap state; most powerful oxidizing agents of all peroxides, decompd by irradiation | Generally not shock sens; deton on heating; peroxyl formic and acetic acids can explode at -20°; stability increases as mw increases |
|                                                                                                         | No information                                                                                               | No information                                                               |
| **Peroxy sulfonic Acids (2), RSO₃—O—OH**                                                             |                                                                                                               |                                                                               |

(continued)
### Table 6 (continuation)

**Comparison of the Properties of Organic Peroxides**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Reactions</th>
<th>Explosiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diacyl Peroxides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sym or unsym diacyl peroxides (1), ( \text{RC(O)}-\text{O}-\text{O}-\text{C(O)R'} )</td>
<td>Low mp solids; rel low decompn temps; autocatalytic and self-accelerating decompn; redn by LiAlH₄; hydrolyzes to corresponding acids; rearrange via an ionization step; sulfonates form adducts with polymers as styrene</td>
<td>Sens to heat, friction and shock; deton on slightest mechanical disturbance; lower members v dangerous; K salts of acylsulfonyl peroxysulfates are explosive</td>
</tr>
<tr>
<td>Peroxydicarbonates (2), ( \text{ROC(O)}-\text{O}-\text{O}-\text{C(O)OR'} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peroxy sulfonylecarbonates (3), ( \text{RSO}_2-\text{O}-\text{O}-\text{C(O)R} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peroxydisulfonates (4), ( \text{RSO}_2-\text{O}-\text{O}-\text{SO}_2\text{R} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peroxyaldehydecarbonates (5), ( \text{RC(O)}-\text{O}-\text{O}-\text{C(O)OR'} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Peroxyesters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peroxyesters (1), ( \text{R} \left( \text{CO}_2\text{R'} \right)_n )</td>
<td>Difficult to prepare because of ready rearrangement or decompn in polar solvents; peroxy sulfonates decomp heterolytically (no free radicals)</td>
<td>Peroxycarbamates are stable, distillable liqs or cryst solids; rapid decompn at 80–140° and violent decompn at 140–180°. Alkylareneperoxysulfonates have low stability and decomp violently at RT within 10 mins</td>
</tr>
<tr>
<td>Peroxy carbonicesters (2), ( \text{ROC(O)}-\text{O}-\text{O}-\text{R} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diperoxyesters (3), ( \text{C(O)}(-\text{O})-\text{O}-\text{R}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peroxy carbamates (4), ( \text{R} \left( \text{NC(O)}-\text{O}-\text{O}-\text{R} \right) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Areneperoxysulfonates (5), ( \text{RSO}_2-\text{O}-\text{O}-\text{R} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Safety.** Since organic peroxides can be initiated by heat, mechanical shock, friction or contamination, an enormous problem in safety presents itself. Numerous examples of this problem have already been shown in this article. Additional examples include the following: methyl and ethyl hydroperoxides expld violently on heating or jarring, and their Ba salts also are extremely expld; the alkylidene peroxides derived from low mw aldehydes and ketones are very sensitive and expld with considerable force; polymeric peroxides of dimethyl ketene, \( \text{CH}_2=\text{C(O)H} \), expld in the dry state by rubbing even at \(-80°\); peroxy acids, especially those of low mw, and diacetyl, dimethyl, dipropionyldine and methyl ethyl peroxides, when pure, must be handled only in small smts and very carefully. Also, dibenzoyl peroxide dust may expld easily by friction or by contamination. Hydrogen peroxide and cmpds contg more than 30% by wt of \( \text{H}_2\text{O}_2 \) are potentially expld (Ref 20)

In order that organic peroxides be produced, shipped and used safely, many investigations have been performed and recommended testing procedures evolved (Refs 4, 12, 18, 22 & 26)

**Analytical.** Since organic peroxides are oxidizing agents the most common chem methods of analysis involve redn of the peroxide group followed by detn of excess reducing agent, or of the oxidized form of the reducing agent. A popular reducing agent is the iodide ion. Its reaction with a diacyl peroxide is illustrated, viz:
\[
R-C-O-O-C-R + 2I^- \rightarrow 2R-C-O^- + I_2
\]

The liberated iodine may be titrated using standard thiosulfate solution, or, in trace analysis, detected by spectrophotometric methods. Other reducing agents commonly used in peroxide analysis are hydriodic acid, ferrous, titanous, stannous, and arsenious ions. Also (recently), triphenylphosphate, which is oxidized to triphenyl phosphine oxide. The excess triphenyl phosphate may be detected gravimetrically, titrimetrically, or spectrophotometrically.

Instrumental methods of peroxide analysis feature polarography, which is used to detect hydroperoxides, peroxyesters, and diazoyl peroxides as well as dicumyl peroxycarbonate in polystyrene. Other techniques include infrared (800 to 900 cm\(^{-1}\)) chemiluminescent analysis for kinetic studies, and chromatography for the identification and separation of peroxides in complex mixtures (Refs. 5, 6, 7, 14, 15, 16, 17, 20 & 21).

Toxicity. The LD\(_{50}\) (oral) values of hydroperoxyalkenals and methyl linoleate hydroperoxide are 450 and 39100 micromoles/kg, respectively, in mice according to Yoshioka and Kaneda (Ref 25). Wolf et al (Ref 24) showed that casein, incubated with H\(_2\)O\(_2\) and freed of excess H\(_2\)O\(_2\) by catalase, is toxic to mice, having negative effects upon growth rate, behavior, and motor coordination. According to Swern (Ref 20) intraperitoneal injection of methyl linoleate hydroperoxide into adult rats is lethal at a level of 150 micromgs/100g. However, diluents such as benz used with comit peroxides are far more dangerous to humans than the peroxides. As a group, the organic peroxides have a low order of human toxicity. However, organic peroxides do have an irritating effect on skin, eyes, nose, and throat. Indeed, cyclohexanone peroxide can cause dermatitis in allergic personnel. The most damaging effect to humans is produced by peroxides entering the eyes. A study of eye damage effects by the US Public Health Service showed that peroxides extensively affect the cornea, iris and conjunctiva of rabbits (Ref 20, p 92). In addition, prolonged exposure to peroxides can cause lung edema.

Recommended precautions for personnel include protective clothing to avoid skin contact, chemical safety goggles, and an inhalation respirator (Ref 27).

Uses. There are about forty to fifty organic peroxides commercially available in more than seventy formulations designed for specific applications which include: (1) initiators for vinyl monomer polymerizations, and copolymerizations of monomers such as vinyl chloride, ethylene, styrene, vinyl acetate, acrylics, fluorolefins and butadienestyrene; (2) curing agents for thermoset polyesters, styreneated alkyls and oils, silicone rubbers and poly allyl diglycol carbonates; (3) crosslinking agents for polyethylene, ethylene-propylene rubbers and styrenebutadiene rubbers; (4) bleaching agents; (5) epoxidizing agents; (6) attempted usage as detonating exsps and exbls by the military; (7) nitrating agents for aromatic amines to achieve a 94% yield of p-Dinitrobenzene (DNB); and (8) catalysts and initiators for such reactions as the chain-chlorination of benzene to produce a highly pure yield of hexachlorocyclohexane (Refs 2, 6a, 13, 14a & 20).


A selected group of organic peroxides which are considered to be of interest in terms of possible usage as expls is presented below under the appropriate organic structure; viz, Hydroperoxides; Organomimetal Hydroperoxides; α-Oxy and α-Peroxy-Hydroperoxides and Peroxides; Ozonides; Peroxides; Peroxy Acids; Diaxyl Peroxides; Peroxy Esters; and Poly Peroxides

HYDROPEROXIDES

Acetylene Hydroperoxide. See Vol 1, A66-L to A67-L

Allyl Hydroperoxide (2-Propenyl Hydroperoxide). CH₂:CHCH₂-O:OH; mw 74.10; OB to CO₂ –172.74%; mp (deton); RI 1.4200. Sol in eth. Prepn is by reacting (with caution) a soin of 10.8g of allyl methanesulfonate in 30ml of methanol and 44g of 30% hydrogen peroxide, with 10.1g of KOH (50% aq) by dropwise addn at 0° in a room illuminated by a photographic red light. Vac distn followed by eth extrn and gas-liquid chromatography prod a 58mg yield. The pure compd is fairly stable to UV light, but deton on heating or in contact with solid alsks

α-Benzenediazobenzyl Hydroperoxide.

\[ \text{N} \equiv \text{NC} \equiv \text{C} \equiv \text{O} \quad \text{mw 228.28; OB to CO}_2 \]

\[ \begin{array}{c}
\text{O} \\
\text{O} \\
\text{H}
\end{array} \]

–210.27%; canary yel ndls; mp 65–6° (decompn). Sol in petr eth. Prepn is by shaking benzalphenylhydrzone suspended in benz (1 g/6cc) with O₂ for about six hrs. Addn of cold petr eth crystd the prod in a 73% yield. Sens to light, the peroxide may expl on standing. It is insens to friction or
impact, but expl on contact with flame, concd sulfuric or nitric acids


2,5-Bis(Hydroperoxy-2,5-Dimethyl)-Hexane. See Vol 2, B144-R

9,9'-Bis(Hydroperoxy)-9,9'-Fluoren+2 Fluorenones (Adduct). See Vol 2, B145-L

tert-Butyl Hydroperoxide. (CH₃)₃C.O.H; mw 90.15, OB to CO₂ =195.2%; colorl, liq, mp 3.8–4.8°; bp 4.5–5.0° at 2mm, 33–4° at 17mm; d 0.896g/cc at 30/4°, RI 1.3983 at 25°. Sol in w. Prepn is by reacting tert-butyl hydrogen sulfate with 30% hydrogen peroxide at 0–5°. After standing overnight at RT the mixt is fractionally distd at 4–5° under vacuum (2mm)(with caution!) to give a 68% yield. Distn at atm press will cause deton. Expl decomp of the hydroperoxide is obtd at 250°


Butyrylhydroperoxide. See Vol 2, B394-L

Cumene Hydroperoxide. See Vol 3, C574-R to C575-R

Diacetylenic Dihydroperoxides. See Vol 5, D1120-R to D1121-L

1,6-Dihydroperoxy-(1,6-Endoperoxy)-Cyclodecane. See Vol 5, D1265-R to D1266-L

Diphenyl Methane Hydroperoxide. See Vol 5, D1464-R to D1465-L

Diacetylenic Dihydroperoxides. See Vol 5, D1120-R

1-Ethoxyethyl Hydroperoxide. See Vol 6, E192-L

1-Ethylcyclohexyl Hydroperoxide-p-Nitrobenzoate. See Vol 6, E224-L

Ethyl Hydroperoxide. See Vol 6, E300-R

Hydroperoxides, Organic (Explosiveness). See Vol 7, H224-R to H227-R

1-Hydroxyethyl Hydroperoxide. See Vol 7, H241-R

Isopropyl Hydroperoxide. (CH₃)₂CH₂.O.O.H, mw 76.12; OB to CO₂ =147.1%; colorl, mobile liq; bp 107–9° (expl decomps just above bp); d 0.8927g/cc at 23/4°; RI 1.8661 at 23°. Miscible with alc, eth and w in all proportions. Prepn is by reacting diisopropyl sulfate with 30% hydrogen peroxide and aq KOH at RT and allowing the mixt to stand for 24hrs. The hydroperoxide is vac distd (Caution!) off at 3mm/21–4°

Ref: S. Medvedev & E. Alexejewa, Ber 65, 133 (1932) & CA 26, 2411–2 (1932)

Methyl Hydroperoxide (Monomethylhydroperoxide). CH₃.O.O.H; mw 48.06; OB to CO₂ =66.58%; colorl liq, mp –72 to –78°; bp 38–40° at 65mm (sl decomp), 90–100° at 760mm (decomp); d 0.9967g/ml at 15/4°; RI 1.3608. Sol in et acet and concd sulfuric acid; sl sol in chl and benz; v sl sol in petr eth. Miscible with w, eth and alc. Prepn is by reacting dimethyl sulfate with hydrogen peroxide and concd KOH
while cooling. A by-product is dimethylperoxide. The monomethylperoxide explodes at about 130° or on warming with some catalysts. It also forms Ba and Ca salts that are w sol and expl when dry.


ORGANOMINERAL HYDROPEROXIDES

TRIETHYLTON HYDROPEROXIDE. (C_2H_5)_3Sn.O.O.H.H_2O_2; mw 272.95; cryst; mp 35—6°. Prepn is by reacting triethyldtin hydroxide with 2 mols of hydrogen peroxide for 20 mins at -60° in the presence of dry magnesium sulfate. The hydroperoxide explodes at 150—180°


Triphenyltin Hydroperoxide. (C_6H_5)_3Sn.O.O.H; white cryst; mp, expls at 75°. Sol in dioxane. Prepn is by reacting 1 g of triphenyltin hydroxide in dry eth (100ml) at RT with 1 ml of 98% hydrogen peroxide. Pptn of the hydroperoxide occurs at -10° in a 45% yield from eth. The expln temp of 75° is very reproducible

Ref: R.L. Danley & W.A. Ave, JOC 30, 3845 (1965) & CA, not found

α-Oxy and α-Peroxy-Hydroperoxides and Peroxides

1,2,3,4-Tetrahydro-1-Naphthyl Hydroperoxide (Tetralinhydroperoxide). CH:CHCCHCH_2

1  O—O.H

CH:CHCCHCH_2 or

O—O.H

mw 164.23; OB to CO -233.82%; yel star-shaped ndlis; mp 56°; d 1.09888/g/cc at 78.8/4°; RI 1.53893 (α), 1.55473 (He). V sol in alks, py and aniline; moderately sol in eth; v sl sol in w. Prepn is by passing air for 50—60 hrs thru coml tetralin at 75°. Vac distn removes the unreac tetralin at 50—60° and 1—2mm. The 15—17% reacted yield is purified by being recryst twice from petr-eth. Deffign occurs above 130°; expln occurs on superheating the hydroperoxide


Bis(1-Hydroperoxycyclohexyl) Peroxide. See Vol 2, B145-R

1,1'-Bis(Hydroperoxycyclohexyl) Peroxide. See Vol 2, B144-L

Bis(Hydroxymethyl) Peroxide. See Di(methylol) Peroxide in Vol 5, D1357

1-Hydroxymethyl Hydroperoxide. See Vol 7, H248-L

Hydroxymethyl Methyl Peroxide.

CH_3.O.O.CH_3.O.H; mw 78.10; oil at RT; bp 41—2° at 55mm; d 0.951g/cc at 15/4°; RI 1.3831. Sol in w. Prepn is by reacting 10% hydrogen peroxide and 1 mwe of dimethyl sulfate with 1 mwe of KOH at RT. The prod is
then extrd with eth using a continuous extractor, followed by vacuum fractional distn to obt a pure yield. The mat is very dangerous to handle, attacking the respiratory organs and producing deep burns on the skin which heal with difficulty. The peroxide is a highly brisant expl which is impact sens when heated
Ref: A. Rieche & F. Hitz, Ber 62B, 2458 (1929) & CA 24, 1078–8 (1930)

**Perparaaldehyde or Monoperaaldehyde.**

\[
\text{H}_3\text{C}\cdot\text{CH}\cdot\text{O}\cdot\text{O}\cdot\text{CH}_3
\]

mw 148.20; OB to CO\_2

\[
-151.15\%; \text{lgt oil; mp 9}^\circ; \text{bp } 45-6^\circ; \text{d } 1.0672 \text{g/cc at } 19.6^\circ; \text{RI } 1.4163 \text{ at } 19.6^\circ. \text{Sol in eth, alc, benz, petr eth and most organic solvs; v sl sol in w. Prep is by cracking the dimer of cyclo-di(\alpha,\alpha'-diethyl ether)-peroxide using a vac distn app. Caution! The residue is extremely sens to mech action and expls on simply touching it. The paraaldehyde expls mildly on heating}

Refs: 1) Beil, not found 2) R. Rieche & R. Meister, Ber 65, 1274–9 (1932) & CA 25, 5906 (1932)

**Per trio xane (Perr trio xymethylene).**

\[
\text{CH}_2\cdot\text{O}\cdot\text{O}\cdot\text{CH}_2
\]

mw 106.11; OB to CO\_2

\[
-75.39\%; \text{colorl oily liq; mp, not avail; bp } 35-6^\circ \text{ at } 12\text{mm}; \text{d } 1.2765 \text{g/cc at } 16.7^\circ; \text{RI } 1.4216. \text{Sol in alc; insol in w. Prep is by reacting P}_2\text{O}_5 \text{ with formaldehyde dissolved in eth at RT for more than several days. Evapn of the eth leaves the prod as a non-vol oil. The compd is extremely expl; it detonates readily on being warmed in a test tube}

Refs: 1) Beil, not found 2) J.F. Walker, "Formaldehyde", Reinhold, NY (1944), 128 3) A. Rieche R. Meister, Ber 66, 720 (1933) & CA 27, 3447 (1933)

**3,3,6,6-Tetrakis(Bromomethyl)-9,9-Dimethyl-1,2,4,5,7,8-Hexaoxaoxane.**

\[
\text{BrH}_2\text{C} \quad \text{O} \quad \text{O} \quad \text{CH}_2\text{Br}
\]

\[
\text{BrH}_2\text{C} \quad \text{O} \quad \text{O} \quad \text{CH}_2\text{Br}
\]

\[
\text{H}_3\text{C} \quad \text{O} \quad \text{O} \quad \text{CH}_3
\]

mw 537.88; OB to CO\_2 -56.52%; crysts; mp 159–62\(^\circ\), decompn > 200\(^\circ\). Sol in acet and dioxane. Prep is by reacting bis[\(\beta,\beta'\)-dibromo-\(\alpha,\alpha'-\)hydroperoxy-isopropyl]-peroxide, obttd by H\_2O\_2 peroxidation of 1,3-dibromoacetone, dissolved in aq acetal with P\_2O\_5 for 20 mins at RT. After sepn from the P\_2O\_5 by filtrn, the prod is cryst from eth/w. The yield is 42%. The peroxide expls on impact or friction, as do the tetrachloro and 9-ethyl-9-methyl analogues
Ref: M. Schulz et al, Ber 100, 2242–9 (1967) & CA 67, 90784 (1967)

**3,3,6,6-Tetramethyl-1,2,4,5-Tetraoxane.**

\[
(\text{CH}_3)_2\text{C} \quad \text{O} \quad \text{O} \quad (\text{CH}_3)_2
\]

mw 148.20; cryst; mp 132–3\(^\circ\) (decomp). Sol in methanol. Prep is by reacting 50% hydrogen peroxide or permonosulfuric acid with acet at RT. The dimeric acet peroxide expls with extreme brisance on impact, friction or rapid heating
Ref: A. Baeyer & V.Villiger, Ber 33, 858 (1900) & CA, not found

**3,6,9-Triethyl-1,2,4,5,7,8-Hexaoxaoxane (Propyli- dene Peroxide)**

\[
(C_2\text{H}_5)\text{HC}
\]

mw 222.30; OB to CO\_2 -151.15%; mobile expl oil; d 1.089g/cc; RI 1.43903. V sol in org solvents; insol in w. Prep is by allowing equimol amts of hydrogen peroxide and n-propyl aldehyde dissolved in ether to stand at RT for several
days, and then treating the soln w/ P₂O₅ at 0°–5° for a longer time. Evpn. of the ether and heating the residue in vacuo gives the peroxide.
The oil is extremely expl and friction sens
Ref: A. Rieche & R. Meister, Ber 72B, 1933–8 (1939) & CA 34, 712–3 (1940)

Tris(Spirocyclopentane)-1,1,4,4,7,7-Hexaoxaonane.

mw 300.42; cryst; mp 166–7°(decomp). Prepn is by reacting 0.52 mole of cyclopentanone with a mixt of 0.43 mole hydrogen peroxide and <0.65 mole of 70% nitric acid at 0°. The prod is a highly brisant expl, v sens to shock, friction and rapid heating

OZONIDES

See in this Vol under Ozonides. The following compds are of special interest:

Benzene Triozonide. See Vol 2, B63

Trans-2-Butene Ozonide.

mw 104.14; colorl gas at RT; bp 15° at 20mm.
Sol in CCl₄. Prepn is by ozonolysis of trans-butene-2 at −70° with a 14.5% yield of the ozonide. Sepn of the product was performed using preparative scale gas partition chromatography at RT. Ignition of the ozonide (for analytical purposes) results in a brisant expln. Isom identification is by infrared and nuclear magnetic resonance spectra
Ref: L.D. Loan et al, JACS 87, 741 (1965) & CA 62, 12993 (1966)

Cyclohexene Ozonide. See Vol 3, C599-R

1,2-Dimethyl-1-Cyclopentene Ozonide.

\[ \text{CH}_3 \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{C} \]
\[ \text{O} \]
\[ \text{C} \]
\[ \text{CH}_3 \]

mw 144.21; mp −13.2°;
bp 58.8° at 15mm
1.0718g/cc; RI 1.4370
at 18.5°. Sol in anhyd petr eth and CCl₄. Prepn is by ozonolysis of 18.5g of 1,2-dimethyl-1-cyclopentene dissolved in 120ml of anhyd petr eth with a mixt of O₃/O₂ contg 5.5% O₃ at −70°. After sohn, the evapn, distn and refractionation of the residue yields 64.3% prod.
The ozonide is stable to vac distn but expls violently at 130° under atm press

1,3-Diphenyl-1,3-Epidoxy-1,3-Dihydroisobenzofuran.

\[ (\text{C}_6\text{H}_5) \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{C}_6\text{H}_5 \]

mw 302.36; cryst; sol in CS₂. Prepn is by exposing a vigorously stirred soln of diphenylisobenzofuran in CS₂ to sunlight for 70 secs.
Vac evapn below 0° yields crystals of the photo-peroxide-ozonide. The compd expls at 18°
Ref: C. Dufrasene & S. Ecary, CR 223, 735–7 (1946) & CA 41, 2413 (1947)

Ethylene Ozonide. See Vol 6, E290-R

trans-2-Hexene Ozonide.

\[ \text{O} \]
\[ \text{O} \]
\[ \text{C}_2\text{H}_5\text{CH}\text{(C}_2\text{H}_5) \]

mw 132.20; colorl gas at RT. Sol in CCl₄. Prepn is by ozonolysis of pentene-2 at −70° with an approx 15% yield of the ozonide. Sepn of the prod in 12.3% yield was performed using preparative scale gas partition chromatography at RT. Ignition of the ozonide (for C and H analysis) results in a brisant expln. Isom identifica-
tion is from infrared and nuclear magnetic resonance spectra

Ref: L.D. Loan et al, JACS 87, 738 (1965)
& CA 62, 12993 (1966)

Isoprene Diozonide. See Vol 7, I136-R

trans-2-Pentene Ozonide.

O

O

mw 118.17; colorl gas at
CH₂CH₃ CH(C₂H₅) O
RT. Sol in CCl₄. Prepn
is by ozonolysis of 10g
of pentene-2 at −70°C
to 60% completion. Prod sepn in 39.7% yield is
obtd with a 20 ft 10% Dow 710 silicone grease
column at temps between 70−110°C (gas parti-
tion chromatography). Ignition of the ozonide
(for C and H analysis) results in a brisant expln.
Isom identification is from infrared and nuclear
magnetic resonance spectra

Ref: L.D. Loan et al, JACS 87, 740−1 (1965)
& CA 62, 12993 (1966)

PEROXIDES

Acetone Peroxides. See Vol 1, A41-R to A45-L

Acetylene Peroxides. See Vol 1, A66-L to A67-L

Ascaridol. See Vol 1, A494-R

1,1′-Bis(Benzoyle peroxy cyclohexane). See Vol 2,
B135-L

2,2-Bis(Butyl peroxy) Propane. See Vol 2,
B137-R to B138-L

Bis(α-Hydroxy-β,β,β-Trichlorethyl) Peroxide.
See Vol 2, B148-R

Bis(Succinyl) Peroxide. See Vol 2, B156-R &
Vol 5, D1512-R

Butadiene Peroxide. See Vol 2, B365-R to
B366-L

Butadiene Peroxide Polymer. See Vol 2, B366-R

Butanone Peroxide Dimer, Methyl Ethyl Ketone
Peroxide. See Vol 2, B375

Cyclohexadiene Peroxide, Polymeric. See Vol
3, C595-L

Cyclohexanone Peroxides. See Vol 3, C598-L
to C599-L

Dianisoyl Peroxide or Anisoyl Peroxide. See
Vol 5, D1152-R to D1153-L

Dibenzal Diperioxide or Dibenzilidene Diperioxide
See Vol 5, D1182-R

Dibenzolsulfonyl Peroxide. See Vol 2, B62-R

Dibenzophenone peroxide Dimer. See Vol 5,
D1184-R

Dibenzoyl Peroxide and Derivatives. See Vol
5, D1186-R to D1188-R

Dibutyl Peroxide or tert-Butyl Peroxide. See
Vol 5, D1197

Di-n-Butyryl Peroxide. See Vol 5, D1200-R
to D1201-L

Di-iso-Butyryl Peroxide. See Vol 5, D1201-L

Dicamphoryl Peroxide. See Vol 5, D1201


Dichloroacetyl Peroxide. See Vol 5, D1204-L

Di(Chlorobenzoyl) Peroxide. See Vol 5, D1208-R

Dicrotonyl Peroxide. See Vol 5, D1216-R

Dicuminoyl Peroxide. See Vol 5, D1216-R

Diethanol-Peroxide. See Vol 5, D1245-R

Diethyl Peroxide. See Vol 5, D1246-R to D1247-L

Diethyl Peroxydicarbonate. See Vol 5, D1247-L

Di-2-Furoyl Peroxide. See Vol 5, D1260-R

2,2'-Difuroyl Peroxide. See Vol 6, F246-R to F247-R

Difurylacryloyl Peroxide. See Vol 5, D1260-R to D1261-L

0,0'-Dimethoxybenzoyl Peroxide. See Vol 5, D1303

Di(Methoxymethyl)-Peroxide. See Vol 5, D1303-R

Dimethylborylmethyl Peroxide. See Vol 5, D1329-R

2,3-Dimethylbutadiene Peroxide, Polymeric. See Vol 5, D1329-R to D1330-L

Dimethyleneperoxidecarbamide. See Vol 5, D1337-R

Dimethyleneperoxide-Ethylamine. See Vol 5, D1337-R

Di(Methylether)-Peroxide. See Vol 5, D1338-L

Dimethylperoxide or Methylperoxide. See Vol 5, D1363

Dipropionyl Peroxide or Propionic Peroxide. See Vol 5, D1492-R

Di(iso-propyl)-Peroxide. See Vol 5, D1500

Ethylethanol Peroxide. See Vol 6, E294-L

Ethylhydroxymethyl Peroxide. See Vol 6, E301-R

Ethylideneperoxide. See Vol 6, E305-R to E306-L

Ethylideneperoxide, Dimeric and Polymeric. See Vol 6, E306

Ethylmethyl Peroxide. See Vol 6, E312-R

Furfuraloxime Peroxide. See Vol 6, F243-R

Hexamethylenediamine Peroxide. See Vol 7, H79-L

Hexamethylenetetramine Triperoxide and Hexamethylenetriamine Triperoxide. See Vol 7, H83-L

7-Hydroxy-1,2-Dioxo-1,2-Dihydro-Naphthalene. See this Vol, N20-R
\( \alpha \)-Hydroxyethylmethyl Peroxide. See Vol 7, H242-L

\( \alpha \)-Hydroxypropylethyl Peroxide. See Vol 7, H248-R

Isoprene(2-Methyl-1,3-Butadiene) Peroxide, Polymeric. See Vol 7, I136-R

Mesityloxideperoxide. See this Vol, M36-L

Phthalyl Peroxide (or Phthalylsuperoxide). (C\(_8\)H\(_4\)O\(_4\))\(_2\); structure unknown; cryst. Expls ca 136° and on contact with concd sulfuric acid Refs: 1) Beil 9, 804 2) H.V. Pechmann & L. Vanino, Ber 27, 1511-12 (1894) & CA, not found

PEROXY ACIDS

Bis(Phthalic Acid) Peroxide. See Vol 2, B156

Peroxyacetic or Peracetic Acid (Acetyl hydroperoxide; Persigl seiure, Acetpersiure or Acetyl-wassersstoffperoxyd in Ger). CH\(_3\)C(O).O.O.H; mw 76.05; OB to CO\(_2\) - 63.12% w white liq; mp 0.1°; bp 20-30° at 10-20mm, 105° (explds violently when heated quickly ca 110°); d 1.226g/cc at 15/4°C; RI 1.3974. V sol in w, eth and sulfuric acid; sol in alc. Prepns is by reacting equimol quants of acetac with 98% hydrogen peroxide in the presence of a catalyst such as 1% sulfuric acid, or by treating acetac with either ozone or O\(_2\) under UV, or by oxidn of dry acetaldehyde in the presence of a catalyst such as Co sulfate, or by reaction of aq hydrogen peroxide with gl acetac and dil sulfuric acid plus propyl acetate with subseq distn of a 25% peroxyacetic acid soln in propyl acetate (Refs 1 to 6 and 9 to 11). Peroxyacetic acid is thermally detonable as a vap, as a soln above 50% in organic media or as a soln above 70 wt % in aq media (Refs 6 & 8). As a liq it is insens to impact (Ref 9), but the solid acid has expld at

Fig 3 Boundaries between detonable and non-detonable regions from 20-120° for various concentrations of peroxyacetic acid in ethyl acetate (A) and acetic acid (B) —20° (Ref 7a). According to Swern (Ref 9) experimentation using blasting caps performed on both eth acet and ace ac solns of peroxyacetic acid has resulted in the data presented in Fig 3

Impurities, such as heavy metal ions, accelerate the decompn and may cause an expln to occur at a lower temp. Open Cup flash pt is 105°F (Ref 12). Since the material is an extremely powerful oxidizing agent it must be handled with extreme caution and kept away from combustible mats (Ref 12)

Tests. Chem analysis consists of reaction with KI soln and titration of the liberated I\(^-\) with Na thiosulfate soln. Instrumental analysis consists of measurement of the carbonyl absorption at 1760cm\(^{-1}\) using an infrared spectrophotometer. This procedure is valid for any physical state or soln strength of the acid (Ref 10)

Toxicity. The peroxy acid is highly toxic and may cause death or permanent injury after very short exposure to small quans (Ref 12)

Uses. Peroxyacetic acid is the most important epoxidation reagent used today because of its economical availability and ease of use with a wide variety of reactants (Ref 10). It also finds wide usage as an organic oxidizing agent (Ref 11)


**Peroxybenzoic or Perobenzoic Acid (Benzoylhydroperoxide or Perobenzoisulfiure in Ger).** C₇H₅.O(O).O.OH; mw 138.12; OB to CO₂ -162.188; wh monocl lfts; mp 41-3°; bp 97-100° at 13 to 15mm (decomps at 80-100° at 760mm) with gas evoln. Sol in acet, benz and chlf; v sol in alc and eth. Prepn is by reacting benzoic acid in methanesulfonic acid with 50-94% hydrogen peroxide for 1-2 hrs at 20-40°. Yield is 75-95% (Ref 6). Other methods of prepn are given in Refs 1-4. The acid explds weakly on heating (Refs 2, 5 & 8). It is a powerful oxid agent which reacts vigorously with reducing mats

**Tests.** It absorbs infrared radiation in soln at 3270-3250cm⁻¹ and as a solid at 3260-3232cm⁻¹ (Ref 7)

**Toxicity.** Peroxybenzoic acid is moderately toxic but does not cause death or permanent injury (Ref 8)

**Uses.** It is used to prep oxiranes and has been used for the epoxidation of over 600 unsaturated compds (Ref 7)

Uses. Its solns are used to epoxidize unsatd organic compds (Ref 7)


Peroxypropionic Acid (Perpropionic Acid or Propionylwasserstoffsuperoxyd in Ger).

C₂H₄C(O).O.O.H; mw 90.105; OB to CO₂

106.34%; colorless; mp 13.5°; bp 23.5° at 20mm; RI 1.4041. Miscible with w, chf, alkyl acetates, alcohols, ketones, etc. Prepns of 99.5% pure acid is by reacting 1 mole of propionic anhydride with 2 moles of 98% hydrogen peroxide at RT using 1% sulfuric acid as a catalyst until equilibrium is achieved. The mixt is allowed to stand for 12 hrs and then distd under a vac of 20mm at 25°. The pure prod is obtbd by fractional freezing and centrifuging (Refs 1 to 4). Peroxy propionic acid puffs off (deflgr) on heating. Although the acid is considered to be more stable than its lower homologues, solns of greater than 60% by wt at 25° in ethyl propionate are unstable to the shock and fire of No 6 blasting caps, decompimg vigorously (Ref 4)


Peroxy succinic acid or Monopersuccinic acid

(HO₂.C₂.H₄.C(O).O.O.H; mw 134.125; OB to CO₂

71.58%; crystals from chlfr and eth; mp 107° (decomp). V sol in alc and acetone; sol in w, eth and ethyl acetate; sl sol in chlfr. Prepns by treating bis(succinic acid) peroxide with w at 30°. Peroxy succinic acid expls on contact with flame and is sl shock-sens (Refs 5 & 6). It decompns on long standing


Phthalonperacid (or Mono-[2-Carboxybenzoyl]-hydroperoxide).

HO(O).C₆.H₄.C(O).O.O.H; mw 182.165; ndles; mp dec ca 110° with gas evoln. V sol in w or eth; sl sol in benz or chlf. Prepns is by reacting phthalic anhyd with an excess of hydrogen peroxide at ~10°. Expls with brisance on rapid heating or on impact

Refs: 1) Bell 9, 804 & [599] 2) A. Baeyer & V. Villiger, Ber 34, 766 (1901) & CA, not found

Terephthalicdiperoxide Acid. C₆.H₄(C(O).O.O.H)₂;

mw 198.17; ndls; mp expls. Sol in alc. Prepns is by reacting terephthalic acid dichloride dissolved in eth with alk hydrogen peroxide soln at 0°. The diperoxide acid explds on heating or from impact. Its Na salt, NaC₆.H₄.O₆, mw 221.121, is also expl

Refs: 1) Bell 9, 844 2) A. Baeyer & V. Villiger, Ber 34, 766 (1901) & CA, not found

Diacyl Peroxides

Acetylbenezoylperoxide and Derivatives. See Vol 1, A54-R to A55-R

2,2-Biphenyldicarbonyl P eroxide (or Diphenoyl Peroxide).

mw 240.24; pale yel cryst; mp, expls at 70°. Sol in methylene chloride. Prepns is by treating a 0.1M soln of phan-threnequinone trimethylphosphate adduct in methylene chloride with 0.0096 mole of ozone at ~75° for 400 secs.
The pptd yield (72% of theory) is filtered and then dried in a current of N₂ at 20° for 1 hr; finally at 0.5 mm. The peroxide can be detoned by impact or on heating to 70°. It is stable at temps below 0°.

Ref: F. Ramirez et al., JACS 86, 4394 (1964) & CA 61, 14569 (1964)

**Bis-o-Azidobenzoyl Peroxide.**

![Structure](image)

mw 324.30; cryst. Sol in aq alc. Prepn is by reacting benzoyl chloride and Na azide in aq et alc at 0°. Recryst from abs et alc. The dry peroxide can be detoned by static electricity


**Bis(3-carboxypropionyl) Peroxide.** See Bis-(succinyl) Peroxide in Vol 2, B156-R to B157-L

**Bisfluoroformyl Peroxide.** FC(O).O.O(O).CF; mw 126.04; color gas at RT. Prepn (with caution) consists of using a clean, dry 3L stainless steel cylinder charged to an initial press of 120 mm with F₂ to a total press of 600 mm with O₂ and then to a total press of 740 mm with CO₂ and finally keeping the cylinder at RT for 6 hrs. The peroxide is extracted from the mix by fractional distn at 0.1 mm and condensed in a trap at −119° in 57% yield. The peroxide expds at 200°. It is stable below 30°.


**Bis(hexahydrobenzoyl) Peroxide or Bis(cyclo-hexanecarbonyl) Peroxide.** See Vol 2, B143-L

**Diacetyl Peroxide or Acetyl Peroxide.** See Vol 5, D1121-R to D1122-L

**Dibenzesulphonyl Peroxide.**

![Structure](image)

mw 314.37; colorl prisms; mp, expds at 53–4°. Prepn is by reaction of benzenesulphonyl chloride with sodium peroxide at 0°. Yield is 10%


**Dibenzyl Peroxide and Derivatives.** See Vol 5, D1186-R to D1188-R

**Di-tert-Butyl Diperoxycarbonate.**

![Structure](image)

(CH₃)₃C.O.O.C.O.O.C(CH₃)₃; mw 206.30; colorl crysts; bp > 95° at 4 mm; RI 1.4106. Sol in eth. Prepn is by reacting a stirred soln of 18g of 71% t-butylihydroperoxide and 16.6g of pyridine in 40 mL eth with 0.08 mole of phosgene introduced at a rate of 6 mmoles/min, while maintaining the temp at 3–5°. Upon standing in the cold for 45 mins the reaction is stopped by the addn of 100 mL of ice-w. Sepn of the eth layer, washing and vac evapn gives the purified 76% yield. The peroxo ester expds with brisance when heated to 135–40°.

Ref: F. Strain et al, JACS 72, 1254–63 (1950) & CA 46, 1984 (1950)

**Di-iso-Butyryl Peroxide.** See Vol 5, D1201-L

**Diacamphoryl Peroxide.** See Vol 5, D1201

**Di-n-Caproyl Peroxide or Bis(n-caproyl) Peroxide.** See Vol 5, D1201-R

**Diacrotontyl Peroxide.** See Vol 5, D1216-R

**Diethyl Peroxydicarbonate.**

![Structure](image)

C₂H₅(OC.O.O.C(O)C₂H₅; mw 178.19; colorl oil; bp 28–35° (decomp); RI 1.4017. Sol in eth.
Prepn is by dropwise addn of a cold aq sodium peroxide (1.0 molar) soln to 1.0 mole of vigorously stirred ethyl chloroformate while maintaining the temp at 6–10°. The mixt is stirred for an addnl half hr after all the sodium peroxide has been added. The oily prod is then sepd, washed with distd w and dried using anhyd Na₂SO₄. An 81% yield is obtd. The frozen ester is sent to the shock from a No 6 elect deton cap, producing a more brisant deton than an equal amt (0.25 lb) of benzoyl peroxide.

Ref: F. Strain et al, JACS 72, 1254–63 (1950) & CA 46, 1984 (1950)

Di-2-Furoyl Peroxide. See Vol 5, D1260-R


Furyl-β-Acrylic Acid Peroxide. See Vol 6, F247-R

Diisopropyl Peroxydicarbonate.

\[(\text{CH}_3)₂\text{CHOCO}_2\text{O}_2\text{CH(OCH(CH₃))₂; mw 206.18; OB to CO₂ 131.92%; colorless crysts; mp 8–10°; bp, rapid decomp at 35–8°; d 1.080 g/cc at 15.5/4°; RI 1.4034. V sl sol in w; miscible with aliphatic and aromatic hydrocarbons, esters, ethers and chlorinated hydrocarbons. Prepn is by slow addn of 112g of pure sodium peroxide soln to 122.6g of vigorously stirred isopropyl chloroformate while maintaining the mixt at 6–10°. The agitation of the mixt is maintained for an addnl half hr subsequent to the complete addn of the sodium peroxide. Purification of the ester requires w washing, drying with anhyd Na₂SO₄, cooling to 10° and filttn to remove the Na₂SO₄. The yield is 81–89%. The ester is considered dangerous. When warmed sl above 10° it undergoes slow self-accelerating decomp which becomes violent under confinement; at 25–30° decomp occurs within 10–30 mins. Addn of 1% aniline, 1,2-di(methoxy)ethane or KI causes instant decomp. N,N-dimethylaniline addn causes an instant expln. Bulk solns of the ester (45%) in benzycyclohexane stored at 5° develop sufficient heat to decomp explosively after a day, and 50–90% solns are impact sens (Ref 1). The solid is normally stored and transported below −18° in loose-top trays.


Dipropionyl Peroxide. See Vol 5, D1492-R

Phthaloyl Peroxide.

\[\text{with 8.3g of Na₂O₂ in 400ml of w at 0°, and then reacting a chlf sln of 20.3g of o-phthaloyl by stirring the mixt for 15 mins while maintaining the temp at 0°. Recryst is from hexane with a yield of 25%. The peroxyxide det at its mp and is probably polymeric.}

Ref: M. Jones & M.R. DeCamp, JOC 36 (11), 1536 (1971) & CA 78, 15697 (1972)

Peroxy Esters

1,1-Dibenzoylsuccinyl Peroxide

\[\text{mw 356.43; cryst; mp 117°. Prepn is by reaction of cyclohexanol (with caution!) with a mixt of 75% H₂O₂ and 0.01 vol % of concd sulfuric acid at 0°. The mixt is allowed to stand overnight under re-}

friguration. The 1-hydroxycyclohexyl 1-hydroperoxide formed (see also Vol 3, C598-L) is then esterified with benzoyl chloride in py at 0°.
The ester expls sharply into flame when heated

**tert-Butyl 1-Adamantanaperoxycarboxylate.**

\[
\text{CH}_3\text{C}_2\text{H}_5\text{C.O.O.C}
\]

MW 252.41; cryst, mp 26–6.5°. Prepn is by reacting tert-butyl hydroperoxide with acyl chloride in the presence of py at 0°, using hexane as the reaction solvent. The ester yield is 89%. It expls at 90–100°. The ester readily initiates the polymerization of methylmethacrylate at three times the rate induced by benzoyl peroxide at 70°.


**tert-Butyl p-Nitroperoxybenzoate.**

\[
\text{O}_2\text{NCHC}_3\text{(C}_2\text{H}_5\text{)} \text{ COO.}
\]

MW 239.275; cryst; mp 78°. Prepn is by reaction of tert-butyl alcohol with (caution!) a mix of 91.5% hydrogen peroxide and 0.01 vol % of concd sulfuric acid at 0°. The mix is allowed to stand overnight under refrigeration. The tert-butylhydroperoxide formed (see Vol 2, B385-L) is then esterified with p-nitrobenzoyl chloride. The ester expls in a flame.


**Butyl Peroxyacetate.** See Vol 2, B387

**tert-Butyl Peroxy Benzoate.** See Vol 2, B387-R to B388-L

**Ethyl Peroxy Acetate.** See Vol 6, E316-R

**Peroxybenzoic Acid, 1,1,4,4-Tetramethylenetetramethylene Ester.** See 2,5-Bis(Benzoyleperoxy)-2,5-dimethyl-hexane in Vol 2, B135-R

**Peroxybenzoic Acid Diester with Bis(1-Hydroxy-cyclohexyl)-Peroxide.** See 1,1'-Bis (benzoyleperoxy)-dicyclohexylperoxide in Vol 2, B135-L

**Peroxybenzoic Acid Diester with Bis(9-Hydroxy-9-Fluorenyl) Peroxide.** See 9,9'-Bis(Benzoyleperoxy)-fluorene in Vol 2, B136-L

**Peroxybenzoic Acid, 9-Fluoranylidene Ester.** See 9,9'-Bis(Benzoyleperoxy)-fluorene in Vol 2, B135-R

**Peroxybenzoic Acid, p-Nitrol, 1,4,4-Tetramethylenetetramethylene ester.** See 2,5-Bis(p-nitrobenzoylperoxy)-2,5-Dimethylhexane in Vol 2, B135-R

**Peroxybenzoic Acid, Cyclohexylidene Ester.** See 1,1'-Bis(Benzoyleperoxy)-cyclohexane in Vol 2, B135-L

**1,1,6,6-Tetakis (Acetyleperoxy) Cyclododecane.**

\[
\text{CH}_3\text{O}_2\text{C} \text{ O}_2\text{O} \text{ O}_2\text{O} \text{ O}_2\text{O} \text{ CH}_3
\]

MW 436.52; rhmb platelets; mp 144–5° (decomp, then deton). Prepn is by reaction of trans-decalhydro-4a-naphthol with 92% hydrogen peroxide to form the tetrahydroperoxide at 0°. Esterification of the peroxide is performed using acetyl chloride. The prod is crysd from ethanol.
The ester deton with brisance on weak friction
Ref: R. Criegee & H. Dietrich, Ann 560, 135-41 (1948) & CA 43, 6189 (1949)

Poly Peroxides

This group consists of polymeric peroxides of indeterminate structure rather than polyfunctional molecules of known structure. The compds listed below are considered to be typical of this group:

Butadiene Ozonide Polymer. See Vol 2, B366-R

Butadiene Peroxide Polymer. See Vol 2, B366-R

Cyclohexadiene Peroxide Polymer. See Vol 3, C595-L

Diethylether Peroxide Polymer. See Vol 5, D1234-L to D1235-L

2,3-Dimethylbutadiene Peroxide, Polymeric. See Vol 5, D1329-R to D1330-L

Dimethylketene Peroxide, Polymeric. See Vol 5, D1348-L

1,1-Diphenyl-ethylene Peroxide, Polymeric. See Vol 5, D1458-R

Ethylidene Peroxide, Polymeric. See Vol 6, E306-L & R

Peroxysuccinic Acid Polymer or Succinyl Peroxide. (Polymer) (Polymerees Succinylperoxyd in Ger). \( \text{O}_2\text{C}-(\text{O})_2\text{C}_6\text{H}_4\text{C}-(\text{O})_2\text{O} \); mw (116.10); OB to CO\(_2\) -82.69%; crystals or amorph; mp (decomps or explds). Prep is by shaking (while cooling) 1 mole of succinyl-

chloride with 1 mole of Na peroxide which is either dissolved in ice w (with a small amt of hydrogen peroxide) or in 10% Na acetate soln. The polymer expls violently at 120° upon slow heating or at 110° when rapidly heated. V sens to friction. It also expls on contact with aniline, concd sulfuric acid or phenylhydrazine. The expln with the latter is so brisant that it will cause a larger quantity of the polymer to detonate at a distance of 2 meters (Refs 3 to 5)
Refs: 1) Beil 2, 612 & [553] 2) L. Vanino
& E. Thielé, Ber 29, 1724 (1896) 3) A.M. Clover & A.C. Houghton, AmChemJ 32, 60
(1904) 4) Ibid, JCS 86, 1, 707 (1904) 5) F. Fichter & A. Frisch, Helv 6, 330 (1923)
& CA 17, 1954 (1923)

Polycyclpentadiene Ozonide. See Vol 3, C602-R

Polycyclpentylidene Peroxide Polymer. See Vol 3, C604-R

Written by H. L. HERMAN

Peroxybutyric Acid. See under Butyrylhydroperoxide in Vol 2, B394-L

Persalites, Gesteins (Gesteins is Ger for Blasting). A group of Ger mining expls manufd from left-over stocks of WWI military expls. Two typical formulations were a) K chlorate 35, AN 43, m-DNT 8, DNN 8, woodmeal 4, and NG 2%; OB to CO\(_2\) -0.3%, Trauzl value 330cc; b) K perchlorate 34, AN 48, m-DNT 10, woodmeal 6 and pulverized coal 2%; OB to CO\(_2\) +1.7%, Trauzl value 325cc
Refs: 1) R. Escales, "Chloratsprengstoffe", Leipzig (1910), 185 2) Naoum, Expls (1927), 127 & 133

Pertit or Pertite. Italian for Picric Acid

Pertuisset Powder. See under Mundell Powder in this Vol, M161-L
PÉTARD. Acronym for Pentaerythritol Tetra-acetate (qv)

Pétard. Fr term for an expl charge designed for demolition purposes. Usually, the pétard consisted of a box (metallic or wooden) containing from 100g up to several kgs of an expl, provided with a primer. In pétards used at the end of the 19th century, the following expls could be found: pressed NC (Ger), Ecrasite (Austria), and Dynamite or Melinite (Fr).

The term pétard was formerly used to designate an ancient device for bursting open gates, barricades, or doors to which it was attached. Basically a case filled with expls, the pétard somewhat resembled a short mortar. A typical pétard might weigh about 60 lbs and have a mouth about 9 inches in diameter.


Pétard d’alarme (Fr). A device classed as an artifice de signalisation sonore and used on railroads for signalling purposes. It consisted of a waterproof container with a mix of 2p Sb sulfide and 1p K chlorate, to which was added a small quantity of powdered glass. After inserting a primer, the ensemble was attached to the upper surface of a rail. When the wheel of a locomotive contacted the primer the charge expld, producing a loud report.

Ref: Pepin Lehalleur (1935), 477

Pétard de mineurs (Fr). See under Miner’s Squib in this Vol, M134-R.

Pétard pour simuler des tirs de batterie (Fr). Pétard simulating the fire of a battery, used in order to deceive the enemy about the location of gun batteries. Most of these pétards consisted of charges of rifle powder enclosed in wood or cardboard boxes, reinforced with cord or wire.

Ref: Pepin Lehalleur (1935), 477

Pétards (ou artifices) pour signaux (Fr). Used during WWI to attract the attention of neighboring troop units or fortifications. The devices consisted of boxes filled with about 400kgs of BlkPdr. They produced a report which could be heard for a distance of 3km, and the smoke produced gave the location of the signalling unit.

Ref: Pepin Lehalleur (1935), 477

Petavel Pressure Gauge. See under Closed Bomb or Vessel in Vol 3, C337-R

Peters’ and Lindsey’s Explosive. AN 75, nitrated wood fiber 20, and oil of mirbane 4% [USP 953798 (1910) & CA 4, 1678 (1910)]. Three variations of Peters’ Explosives are: 1) AN 30, NC 30, K chlorate 30, and oil of mirbane 10% [USP 988590 (1911) & CA 5, 2179 (1911)]; 2) AN 50, K chlorate 30, oil of mirbane 10, and woodmeal 10% [USP 991232 (1911) & CA 5, 2332 (1911)]; 3) AN 67, nitrated woodfiber 10-20, Na chloride 20, asphalt soln in MNPh 2, and Ca carbonate 1% [USP 994273 (1911) & CA 5, 2557 (1911)]

PETN. Acronym for Pentaerythritol Tetranitrate. See under Pentaerythritol and its Derivatives in this Vol.

Petragite. An expl invented by Doutrelepton and Schreiber in the 19th century. It contained K nitrate 56.4, Nitromolasses 38.6, and nitrated sawdust 5.0%.

Ref: Daniel (1902), 612

Petralite. An expl invented in Hungary in the 19th century by Liesch and Prohaska. It contained K nitrate 64, nitrated sawdust 30, and Amm carbonate 6%.

Ref: Daniel (1902), 612

Pétralithe or Pétralite (Fr). An expl submitted to the Commission Francaise des Substances Explosives in 1880: NG 60, K or Na or Amm nitrate 16, charcoal (specially prepd) 16, lignite.
6. Ca carbonate 1%, and spermaceti 1%. Its manuf was authorized by the Commission
Refs: 1) Commission des Substances Explosives, MP 1, 459 (1882) 2) Daniel (1902),
612 3) Guia, Trattato VI (1) (1959), 345

Petrin. See as Pentaerythritol Trinitrate under
Pentaerythritol and its Derivatives in this Vol

Petrin Acrylate (Pentaerythritol Trinitroacrylate,
Trinitroxypentaerythritol Acrylate). C₆H₁₁N₃O₁₈,
CH₂ONO₂
CH₂=CH–CO₂CH₂C–CH₂ONO₂
CH₂ONO₂
mw 325 (monomer), cryst., OB to CO₂ — 54%,
mp 78 — 79°, Q₆ 2923cal/g, Q₇ 791cal/g. Its
principal use is as an ingredient of composite
rocket propelsn (see below) (Ref 4)
Prepn. The original synthesis for PETRIN
acrylate employed trifluoroacetic anhydride
and glc acrylic acid as the acylation agent for
PETRIN. These two materials were charged to
a reaction vessel and the initial reaction was
controlled by the slow addition of PETRIN at
a temp of 10 — 15°. Following a period of one
hour, the batch was drowned in w, ppg the
PETRIN acrylate. This solid was sepd by fltn,
dissolved in chl, and neutralized in soln with
Na bicarbonate. The product was then crystd
during a period of 16 hours at 0° and dried
under vac to remove traces of solvent. The yield
for this process was about 60%
A significant improvement in yield (to about
74%) and purity (approx 98%) was realized by the
substitution of methanol for chl and crystn
of the product from the soln without neutral-
ization, residual acid being removed by washing
the filter cake with w
Because of the high cost and hygroscopic
nature of trifluoroacetic anhydride, a new
process, based on dimethylaniline and acryl
chloride, was considered. Yields averaged 46%
and product purities averaged 93.5% (Refs 2, 3
& 4):

HOCH₂C(CH₂NO₂)₃ + CH₂ = CHCOCI +
pentaerythritol acryl
trinitrate (PETRIN) chloride
C₆H₇N(CH₃)₂ → C₆H₇N(CH₃)₂HCl +
dimethyl dimethylaniline
aniline hydrochloride
O
(O₂NOCH₂)₃CCH₂OCCH = CH₂
pentaerythritol trinitrate
monocrylate (PETRIN acrylate)

PETRIN acrylate propels. PETRIN acrylate
could be used as a monoproplnt because it has
a specific impulse of 214 lb-sec/lb and a burning
rate of 0.2 inch/sec. The addition of an oxidizer
increases both the impulse and burning rate.
A typical compn is as follows:

<table>
<thead>
<tr>
<th>Composition</th>
<th>NM*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETRIN acrylate</td>
<td>34.3 (binder)</td>
</tr>
<tr>
<td>(&gt; 97% purity), %</td>
<td></td>
</tr>
<tr>
<td>Triethylene glycol trinitrate</td>
<td>11.8 (plasticizer)</td>
</tr>
<tr>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Glycol diacrylate, %</td>
<td>2.9 (crosslinker)</td>
</tr>
<tr>
<td>Ammonium perchlorate, %</td>
<td>51.0 (oxidizer)</td>
</tr>
<tr>
<td>Hydroquinone, %</td>
<td>0.014 (polymerization inhibitor)</td>
</tr>
</tbody>
</table>

*Measured specific impulse 238 lb-sec/lb, at d 1.3g/cc
See also under Pentaerythritol Trinitrate in this Vol

Refs: 1) Anon, “Process for the Manufacture of
Pentaerythritol Tetrinitrate Monocrylate and
Petrin Acrylate Propellants”, Rohm & Haas Co,
Redstone Ars, Ala (12 March 1956) 2) R.F.
Precelk, USP 3116597 (1964) 3) R.F. Gould,
Ed, “Advanced Propellant Chemistry”, Advances
in Chemistry Series 54, American Chemical
Society, Washington, DC (1966), 99—100
4) Anon, “Explosives Series, Properties of
Explosives of Military Interest”, EngrDesIndub,
AMCP 706-177 (1971), 269—71

Petrofacteurs. Chlorate and perchlorate expls
used in Austria before and during WWI. Typical
formulations include: 1) MNB 10, Sb sulfide 3,
K chlorate 67, and K nitrate 20%; 2) DNB 10,
Amm perchlorate 35, Na nitrate 45, sawdust 8,
and vaseline 2%
Refs: 1) Daniel (1902), 613 2) Colver
(1918), 143
Petroklastit or Haloklastit. Ger expl designed for blasting soft materials such as rock salt, etc. It contained Na nitrate 69, K nitrate 5, S 10, coal tar 15, and K dichromate 1%. It was less sensitive to impact than Blk Pdr, and its strength (as detd by the Trauzl test) was about 145% that of Blk Pdr. It was less hygroscopic than Blk Pdr, and could be ignited at 350°.

Ullmann (Ref 3) gives its compn as: Na nitrate 70, K nitrate 5, tar 15, and S 10%
Refs: 1) Daniel (1902), 612 2) Marshall 1, 89 (1917) 3) Ullmann 4, 2nd Ed (1926), 780 4) Stettbacher (1933), 111

Petroleum, Nitrated. The nitration of petroleum generally produces either brown, non-cryst solids or liq products that are expl.

The first attempts to nitrate petroleum were made in Russia at the end of the last century by Konovaloff, Walden, and others. They used dil nitric acid alone under press, and obtained nitrated products in very low yields. None of these expls was on an industrial scale.

Edelmann and Filiti patented in 1902 (Ref 1) a nitrating method using mixed nitric-sulfuric acids. The use of petroleum fractions having a d of 0.87 g/cc and bp's between 270–380° was recommended. The hydrocarbons were added gradually to a mixt of the concd acids maintained at a low temp. During the reaction the temp was not allowed to exceed 80°. The most suitable proportions were: for 1 pt of petroleum fraction, 3 pt of concd nitric acid, previously mixed with 15 pt of fuming sulfuric acid. When the nitration was completed, the mixt was diluted with a large vol of cold w. This produced a ppt of the nitrated product, while the un-nitrated oil floated to the top of the acid-w soln. After washing, yields ranged from 30 to 90%, depending on the crude oil used. It was found that more stable products of nitration were obtained when the crude oil was purified prior to distn, by treatment with a small quantity (about 1%) of concd sulfuric acid, followed by washing. The nitrated products proved to be expl, sol in most org solvents, and good gelatinizers for NC. No practical application has been made of this patent.

In 1913, A.S. Flexer of Vienna patented a process for the manuf of nitrocomps by the action of concd nitric acid on a mixt of illuminating oil and wood tar. The oily compds thus produced were highly expl (Ref 3).

Freund (Ref 2) nitrated a fraction of Galician petroleum (from Borislaw), bp 270–380°, d 0.858–0.870 g/cc (previously purified by treatment with 1% concd sulfuric acid), and obtained a red-brown powder with a N content of about 6.8%.

Kharichkov (Ref 3) nitrated some machine and spindle oils, obtained from Russian "mazut" (qv) by moderately warming with concd nitric acid (d 1.50 g/cc), and obtained thick, very viscous syrups, sol in benz, which can be used for separating them from the excess oil. By dissolving the nitrated products and pptg w, he was able to obtain several fractions of varying d and N content. For example, one of the fractions contained N=6.66%, its d was 1.103 g/cc and its mp 52–54°.

Many other investigators have nitrated petroleum fractions. These are detailed in Ellis' two vols (Ref 4)

Petrolit. An old (1876) Dynamite contg NG 60, K or Na nitrate 16, carbon 16, sawdust 6, cetyl palmitate 1, and Na carbonate 1% (Ref 2)

The same name was applied to a Ger chlorate expl introduced during WWI. It consisted of K chlorate, nitrocompds, kerosene, and neutral salts, and was considered a dangerous mixt (Ref 1)
Refs: 1) Marshall, Dict (1920), 74 2) A. Pérez Ara (1945), 331

Petronel (Poitrinale). See under Bullets in Vol 2, B324-R

Pettingill. A powder, patented in Engl in 1895, contg crude salt peter 63, coal dust 20, crude S
15, and wood flour 2%. It was prep'd by adding, with agitation, the required amt of coal dust to a hot satd soln of salt peter. After the w was evapd by heating, S was added and thoroughly blended and then, finally, the wood flour.

Ref: Daniel (1902), 613–14

Pettman Cement. Pettman Cement (PC) is described briefly in Vol 2, C126-R. This water-repellant cement originally consisted of methylated spirit, Stockholm tar, Venetian red, and shellac. It was used as an adhesive in making flares and signals and is mentioned in an early BritP (Ref 1).

In the USA, PC is used in the loading and assembly of ammo as a fastener to secure both threaded and unthreaded parts, such as booster cups and joints. Accdg to Ohart (Ref 5), upon drying, PC “sets up”, becoming hard and making a reliable joint. Shellac is used to coat cavities to be loaded with BlkPdr such as delay element cavities and time train ring grooves.

Shellac (described in Vol 6, G187-L under Gum Lac) became a strategic material during WWII, and a mixt of rosin and ethyl cellulose was substituted for it. The modified cement possesses drying time and waterproofing props similar to those of the original PC (Refs 2 & 3).

Two types of PC exist for mil purposes. Type A PC is prep'd by mixing pine tar and alc, adding shellac and stirring well. After the mixt has been allowed to stand for about 20 hrs, it is stirred thoroughly and iron oxide is added in small portions until a product of uniform consistency is obt'd.

Type B, a modified PC, is prep'd by mixing alc and ethyl cellulose until a clear soln is obt'd, then adding rosin and mixing until it is dispersed. The pine tar is then added with thorough stirring. Finally, iron oxide is added in small portions with continuing stirring until uniform consistency is obtained.

The automated inspection for deposition of the solids content of PC is a critical operation in the manufg process of various munition items. Electrical continuity techniques have been used to determine the extent of deposition with standing time (Ref 9). New techniques have also been developed to stabilize PC used for coating propellant grains in rocket motors. These techniques gave a homogeneous mixt of the cement maintainable over considerable time periods, resulting in increased item reliability and safety (Ref 8). Many adhesive systems, including several commercial paints have been suggested as possible replacements for PC (Ref 8).

US Mil Spec JAN-C-99 (Ref 4) contains the requirements for each ingredient of PC, including a viscosity test for the finished PC as well as std tests for the ingredient under several Fed Specs. However, some of these Fed Specs are outdated and are currently being replaced. A recent PATR (Ref 8) made recommendations to update JAN-C-99.

The present US Mil formulations for PC are (Ref 4):

<table>
<thead>
<tr>
<th></th>
<th>Type A (PC)</th>
<th>Type B (modified PC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide(a), %</td>
<td>50 ± 3</td>
<td>33 ± 2</td>
</tr>
<tr>
<td>Alcohol(b), %</td>
<td>20 ± 2</td>
<td>19 ± 2</td>
</tr>
<tr>
<td>Shellac(c), %</td>
<td>18 ± 2</td>
<td>--</td>
</tr>
<tr>
<td>Pine tar(d), %</td>
<td>12 ± 1.5</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>Rosin(e), %</td>
<td>--</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>Ethyl cellulose(f), %</td>
<td>--</td>
<td>1 ± 0.5</td>
</tr>
</tbody>
</table>

(a) Over 96.5% shall be 44 microns in particle size, detd gravimetrically by burning off the combustible material.

(b) Grade 2 alc or a mixt of ethyl and methyl alc's; shall cont a mixt of 5% methanol and no benz; detd by wt loss after drying at 75° for 6 hrs for Type A and 2 hrs for Type B.

(c) Detd by wt of residue from repeated extrn with carbon tetrachloride.

(d) Type A, subtract from 100 the sum of a, b and c.

(e) & (f) Type B, subtract from 100 the sum of a and b.

Written by H. T. LEE


PETX. Code name for Tetrakis(nitraminomethyl)-methane or Pentaerythrityltetrazakis(nitramine) (qv in this Vol)

Peyton Powder. According to Daniel (Ref 1), this was a smokeless powder patented in Engl in 1895 and later manufd in the USA by the California Powder Co. It contd a jelly consisting of 40p of NC and 38p of NG (acet was used as solvent), blended with 22p of other oxidizer ingredients

According to Colver (Ref 2), the compn of one of the Peyton powders was NC (sol) 40, NG 40, and Amm Picrate 20%

Refs: 1) Daniel (1902), 614 2) Colver (1938), 341

P Gunpowder. One of the varieties of Pebble Powder (Poudre cailloux in Fr) manufd in Engl beginning 1865. It contained 176 grains per kg. Another variety, called P2 Gunpowder, containing 15 to 16 grains per kg, was used in larger cal guns. See also under “P” (Pebble Powder) in this Vol


PGX. Code name for 1,5-Dinitro-3-methyl-3-methylideninitramine-1,5-diazapentane

P.H.E. (Plastic High Explosive). Developed during WWII by the Brit for demolition purposes. It was a putty-like brownish material consisting of RDX 88, oil 11.6 and lecithin 0.6%, and had a d of ca 1.5g/cc. Lecithin was added to prevent the formation of large RDX crystals on prolonged storage. See also Composition C Type Explosives in Vol 3, C484-L to C488-R

Ref: Anon, “Allied and Enemy Explosives”, Aberdeen Proving Ground (1946), 125

Phenacyl Azide. See w-Azidoacetophenone in Vol 1, A47-R

Phenacyl-3,5-Dinitrosalicylate.
\[ \text{C}_8\text{H}_5\text{CO.CH}_2\text{O}_2\text{C.C}_8\text{H}_3\text{(OH)(NO)}_2_2 \]

mw 346.25. N 8.1%, OB to CO\(_2\) -124.76%. Was prep'd in 1931 and found to be a powerful expl

Ref: Ko-Chung Chen, TransSciSocChina 7, 73-80 (1931) & CA 26, 49 (1932)

PHENANTHRENE AND DERIVATIVES

Phenanthrene (o-Diphenylenediethylene).

\[
\begin{array}{cccccc}
7 & 8 & 9 & 10 \\
6 & 5 & 4b & 4a & 3 & 2
\end{array}
\]

mw 178.22; colorless plates from alcohol; mp 100\(^\circ\); bp 340\(^\circ\). Obttd by fractional distn of high-boiling coal tar oils with subsequent extrn from alc (Ref 1)

Under hyper-pressure conditions combined with shearing stress, Gonickberg et al, in 1968, observed expl behavior by both phenanthrene and perylene at pressures in excess of 50 kilobars (Ref 14), far above any practical value for munitions use. Much earlier, Spica proposed the addition of 2.5% of phenanthrene as a stabilizing and anti-corrosion agent for both NG and NC smokeless powders (Ref 5). Subsequently, Tonegotti found that the stabilizing properties of phenanthrene for NG were intermediate between those of diethylphenylurea (Centralite) and asym-diphenylurea (Acardite) using the test methods of Taliani and Thomas (Ref 8). DeMent has applied for a patent for the use of phenanthrene as a fluorescing agent in smoke used for military signaling (Ref 9)

Phenanthrene Dioxide. \[ \text{C}_14\text{H}_{10}2\text{O}_2 \]

Harries and Weiss in 1905 reported that the ozonolysis of phenanthrene in chl soln produced a crystn, expl dioxide (Refs 2 & 4). Subsequently, very detailed studies of the ozonolysis reaction of phenanthrene by three different groups of investigators failed to confirm the existence
either of a diazonide, or of any products of this reaction that would explode under heating, friction or impact (Refs 10, 11, 12 & 13)

1,2,3,4a,4b,5,6,10,10a Decahydro-1,4a-Dimethyl-7-(1-Methylthethyl)-Phenanthrene-1-Carboxylic Acid Polinitrate (Abietic Acid Polinitrate).

![Chemical Structure](image)

Yellow, amorph solid which expids on heating (Ref 6)

Sodium-1,2,3,4a,4b,5,6,10,10a Decahydro-1,4a-Dimethyl-7-(1-Methylthethyl) Phenanthrene-1-Carboxylate (Sodium Abietate).

![Chemical Structure](image)

It has been patented as a 0.1% coagent for aluminum used in expl slurries to improve detonation sensitivity (Refs 3 & 15)

3,4,8-Trimethoxyphenanthrene-5-carboxylic acid azide.

![Chemical Structure](image)

mw 286.17, N 14.68%, OB to CO₂ -159%; decomps at 65° (heated slowly) but expids at 80° when immersed in a bath at that temp (Ref 7)

Numerous molecular compds of phenanthrene and its derivatives have been reported with perchloric acid, PA, stypnic acid, sym-TNT, sym-TNB, and Tetryl. These compds are useful for identification purposes because many have sharp melting points but none have been reported to be expl.


9,10 Phenanthrenequinone and Derivatives

9,10-Phenanthrenequinone (9,10-Diosphenanthrenedihydride-9,10). Mw 208.2; orange needles; mp 209°, sublimes above 360° to give orange-red plates. Obt from phenanthrene by chromic acid oxidn in acetic acid (Ref 1)
2-Azidophenanthronequinone.

mw 249.14, N 16.86%, OB to CO₂ –189%, cinnabar-red, or sometimes, copper-bronze colored leaflets. When heated dry in a test tube it at first darkens at 175°, melts at 186°, then on further heating, during emission of a thick brown smoke, in addition to exploding it deposits a brown sublimate in the cold parts of the tube (Refs 3 & 7)

4-Azidophenanthronequinone.

mw 249.14, N 16.86%, OB to CO₂ –189%, garnet-red, irregularly star-shaped crysts that on heating expld before melting (Refs 4 & 8)

Phenanthronequinone-2,7-diazide.

mw 290.22, N 28.96%, OB to CO₂ –149%, brown crysts, mp 248° with expln. When mixed with concd sulfuric acid it explds, deflagrating with incandescence and emission of a thick brown smoke. It is stable to impact (Refs 5 & 9)

Phenanthronequinone-4,5-diazide.

mw 290.22, N 28.96%, OB to CO₂ –149%, mp 160°, on further heating it explds. It dissolves in concd sulfuric acid with the emission of nitrogen, but without violent decompn (Refs 5 & 9)

4-Nitrophenanthronequinonemonoxime
mono semi carbzone.

mw 325.27, N 21.53%, OB to CO₂ –155%, yellowish-green cryst powd, mp 240° (dec). Schmidt et al observed that, "When one heats somewhat larger amounts of this preparation a lively detonation occurs. This was, for example, the case when the carbon and hydrogen determination by combustion of the substance in a little boat was carried out in the usual way. The detonation was so forceful that the cupric oxide was shot out of the combustion tube. Because of the all-too-great danger accompanying a repetition of the intended combustion, we had to be satisfied to determine the nitrogen content of the compound. To this end a suitably small amount of the substance was mixed with a suitably larger charge of copper oxide and then the Dumas nitrogen determination was carried out in a long combustion tube. Handled in this way the substance was completely decomposed, slowly, without any danger." (Refs 2 & 6)
The foregoing quotation points out that the publication of routine elemental analytical combustion results can serve to separate stable compds from those that expld before pyrolyzing

Written by D. J. VEAL


Phenotedines. See under Aminophenotedes and Derivatives in Vol 1, A240-R

Phenetole And Its Derivatives

Phenetole (Ethylphenylether, Phenylethylether). C₆H₅OC₂H₅, mw 122.16, oily liq, mp -30°, bp 171-73°, d(20/4°) 0.9676/g/cc, Rf 1.507. Practically insol in w, freely sol in alc, ether.

Can be prepd from phenol or its salts by the use of the following ethylating agents: ethyl chloride, ethyl bromide, ethyl p-toluenesulfate, dimethyl sulfate or triethyl phosphate. Combustible.

On nitrations it yields products which are suitable for use in expl comps


Mononitrophentolatoes. C₂H₅OC₆H₄NO₂, mw 167.17, N 8.4%, OB to CO₂ -167.5%

o-Mononitrophentolate. Yellowish oily liq, mp 2.1°; bp 267-8° at 757mm, 275° at 760mm; d 1.1903/g/cc at 15°; Rf 1.5425 at 20°. Nearly insol in w, sol in alc and eth. Qₜ 1021kcal/mole


m-Mononitrophentolate. Light yel crs, mp 36°, bp 284° decomp, Qₜ 1009.4kcal/mole

Dinitrophentolate. C₂H₅OC₆H₄(NO₂)₂, mw 212.16, N 13.2%, OB to CO₂ -113.1%

2,3-Dinitrophentolate. Light yel leaflets from alc, mp 101°. Was prepd by Blanksma (Ref 2) by the deamination of 2,3-dinitro-4-amino-phenol.

Refs: 1) Bell 6, 251  2) J.J. Blanksma, Rec 27, 50 (1908)

2,4-Dinitrophentolate. Colorl leaflets from dil alc; needles from w or alc; mp 86-7° subl, decomp at higher temps. Can be prepd by the nitration of phenol with fuming nitric acid or by other methods given in Ref 1. Desvergnes (Ref 3) gives a detailed description of its lab scale prepn. The Japanese (Ref 4) prepd it on a large scale by the reaction of dinitrochlorobenzene with alc NaOH:

(O₂N)₂C₆H₅CH₃ + NaOH + C₆H₅OH →

(O₂N)₂C₆H₅OC₆H₄ + NaCl + H₂O

The resulting dinitrocompd was used for the prepn of the trinitrocompd (see below), used to some extent as a military expl

Refs: 1) Bell 6, 254, (126) & [242]  2) A. Cahours, AnnChim(Paris) [3], 27, 465 (1849)  3) L. Desvergnes, MP 19, 285-90 (1922); MonistScientQuesneville [5], 14, 254 (1924)  4) Anon, PB Rept No 50394 (1946), 28-30

2,5-Dinitrophentolate. Crystals, mp 96-98°; was prepd by deamination of 2,5-dinitro-4-amino-phenol.

Refs: 1) Bell 6, [245]  2) F. Reverdin & H. Roethlisberger, Helv 5, 303 (1922)
2,6-Dinitrophenetole. Colorless needles, mp 57–8°; was prepared by treating Ag 2,6-dinitrophenetole with ethyl iodide, or by other methods detailed in the ref
Ref: Beil 6, 257 & (127)

3,5-Dinitrophenetole. Colorless crystals from alc; mp 96–7°; was prepared in small yield from Na ethylate and 1,3,5-TNB
Ref: Beil 6, 258

Trinitrophenoles. C₆H₄OC₆H₅(NO₂)₃, mw 257.0, N 16.3%, OB to CO₂ –77.8%

2,3,4-Trinitrophenole. Colorless crystals from alc; mp 117°; can be prepared by nitrating 2,3-dinitrophenole with mixed nitric-sulfuric acid
Refs: 1) Beil 6, 264 2) J.J. Blanksma, Rec 27, 49–51 (1908)

2,3,5-Trinitrophenole. Light yel crystals; mp 80°; can be prepared by nitrating 3,5-dinitrophenole with mixed nitric (d 1.44g/cc) and concd sulfuric acids
Refs: 1) Beil 6, 264 2) J.J. Blanksma, Rec 24, 41 (1905)

2,4,6-Trinitrophenole (TnPht; Ethyl Picrate; Aethyl-[2,4,6-trinitrophenyl]-ether, Pigrin- saureethylather or Aethylpikrat in Ger; Keineyaku or Keyneyaku in Japanese).

C₆H₄N₃O₇, (O₂N)₂C₆H₅OC₂H₅, mw 257.16, N 16.3%, OB to CO₂ –77.8%, yellowish crystals, mp 78–80°, Q 93.9 kcal/mole

TnPht can be prepared by nitrating of 2,4-dinitrophenole or by other methods given in Refs 1 & 10. Desvergne (Ref 4) gives a detailed procedure for its lab prep:

Dissolve 53g of 2,4-dinitrophenole in 175g of concd sulfuric acid with agitation. Add 62% nitric acid so that the temp rises rapidly to 30°. Continue the addition, while maintaining the temp between 30–40° (by cooling), until a total of 40/75g of nitric acid has been added. Pour the resulting yellow slurry into about 1500g of cold w, filter and wash the crystals with cold w and dry. This method yielded 61.8g of product, 96% of theoretical, mp 78.5°.

Nitrating on an industrial scale at “la Poudrerie de Bouchet” gave a product with mp 76–77° in 78% yield. The Japanese manufd it as a mil exp by nitrating 2,4-dinitrophenole (Ref 9)

The solubility of TNPh in grams per 100g of various solvents was detd by Desvergne (Ref 4, pp 255–6), and are given below in rounded figures:

Water. 0.013 at 15°, 0.044 at 50° and 0.354 at 100°. TNPh is slowly saponified by hot w with the formation of iso-Picric Acid, in a manner similar to the saponification of 2,4,6-Trinitroanisole

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ethyl Acetate</th>
<th>Acetone</th>
<th>Ethanol (96%)</th>
<th>Ethanol (abs)</th>
<th>Methanol</th>
<th>Benzene</th>
<th>Chloroform</th>
<th>Ether</th>
<th>Pyridine</th>
<th>Carbon Disulfide</th>
<th>Carbon Tetrachloride</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°</td>
<td>36.53</td>
<td>120.3</td>
<td>1.20</td>
<td>1.67</td>
<td>3.99</td>
<td>49.2</td>
<td>20.79</td>
<td>3.79</td>
<td>185.3</td>
<td>0.43</td>
<td>0.667</td>
<td>30.8</td>
</tr>
<tr>
<td>50°</td>
<td>185.2</td>
<td>410.5</td>
<td>7.82</td>
<td>9.32</td>
<td>24.0</td>
<td>297.3</td>
<td>174.7</td>
<td>7.66</td>
<td>327.9</td>
<td>1.69</td>
<td>6.43</td>
<td>163</td>
</tr>
</tbody>
</table>

Explosive Properties. 2,4,6-TNPh is an expl, almost as powerful as TNT and slightly less powerful as PA (as detd by the Trauzl test). Its rate of detonation, as detd by the Dauthrie method, was about the same as that of TNT (6880m/sec). Its sensitivity to impact, as detd in Fr, was considerably lower than for PA, but according to tests conducted in Engl, TNPh was more sensitive than PA (Ref 8). When pellets of TNPh (d 0.25g/cc) were fired in a manometric bomb, the pressure developed was 2490kg/sq cm, as against 3230 for PA

When used as a booster in a 75mm shell loaded with “Schneiderite”, the TNPh gave the same performance as cryl TNT

Uses. The possibility of using TNPh as a bursting charge in projectiles was studied in Fr as early as 1917. Several mixts contg TNPh were prepd and tested, eg: 1) TNPh 30, PA 70%; 2) TNPh 70, Na nitrate 30%; and 3) TNPh 60, AN 40%. The third compn was loaded into shells at d 1.5 to 1.6g/cc, and gave very good fragmentation results. It was used as sensitive to impact as PA, and the pressure developed in a manometric bomb at a loading d of 0.25g/cc was 2741kg/sq cm vs 3230 for PA
The Japanese used TNPh during WWII for cast loading some of their projectiles, and considered it a suitable substitute for TNT, which was then on the critical list because of a shortage of toluene (Ref 9).

Note: According to Brady and Horton (Ref 6), TNPh forms an unstable addition compd with 2,4,6-Trinitroanisole (TNAn) consisting of 2 moles of TNPh and 3 moles of TNAn. The mp of this compd is about 40°.

When a satd soln of TNPh in pyridine is cooled, orange crystals corresponding to the compd C₆H₅(OH)(NO₂)₃.2C₂H₅N are deposit-ed, mp 84.5 to 85.5°. When heated to a higher temp, the crystals dehydrate (Ref 4, p 257)

Refs: 1) Beil 6, 264, 290, (140) & [281] 2) P. Austen, Ber 8, 666 (1875) 3) M. Marquerot et al, BullFr [4], 27, 106 (1920)

2,3,5,6-Tetranitrophenetole. (O₂N)₄C₆H₅HOC₆H₅, mw 302.18, N 18.5%, OB to CO₂ 52.9%, light yel crystals from alc, mp 115°. Can be prepd by heating a mixt of 3,5-dinitrophenetole, concd nitric and concd sulfuric acids on a w bath. It can also be prepd by the nitration of 2,3,5-Trinitrophenetole. It is an expd, and was patented in Ger during WWII (Ref 3) for use in initiating compns

Refs: 1) Beil 6, 293 & (142) 2) J.J. Blanksma, Rec 24, 42 (1905) 3) C. Claessen, GerP 288655 (1915); ChemZtr 1916, 1, 240

Phenixsprengstoffe. Mining expls patented in 1899 by the Sprengstoffwerke Dr Nahnse & Co in Hamburg, Ger. Five typical compns are shown in Table 1:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Composition %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>NG</td>
<td>25</td>
</tr>
<tr>
<td>K nitrate</td>
<td>34</td>
</tr>
<tr>
<td>Na nitrate</td>
<td>1</td>
</tr>
<tr>
<td>Sawdust</td>
<td>40</td>
</tr>
<tr>
<td>Rye flour</td>
<td></td>
</tr>
</tbody>
</table>

Composition No 5 had a Q₅ of 780cal/g and an expln temp of 2125°.

Refs: 1) Daniel (1902), 449 2) Gody (1907), 715 3) PATR 2510 (1958), Ger 130-R

**PHENOL AND ITS DERIVATIVES**

**Phenol** (Carbolic, phenic or phenyllic acid; Hydroxybenzene; Oxybenzene). C₆H₅OH, mw 94.11; white, cryt mass or colorl, accecl crytsw which turn pink or red if not perfectly pure or if under the influence of light; absorbs w from the air and liquifies; distinctive odor; sharp burning taste; mp 42–43°; bp 182°; flash pt 79°; d 1.071 g/cc; combustible, autoignition temp 1319°F. Sol in alc, w, eth, chf, glycerol, CS₂, petrolatum, fixed or volatile oils and alkaies. Obtained from coal tar, or made by fusing Na benzene sulfonate with NaOH, or by heating monochlorobenzene with aq NaOH under high press. The cryt article of commerce contains at least 98% phenol. Modern manuf processes are described in detail in Ref 2. Highly toxic by ingestion, inhalation and skin absorption. Strong irritant to tissue. Tolerance 5ppm in air (Refs 3 & 4)

Phenol has been used as a starting material for the prepn of such expls as Dinitrophenol, Trinitrophenol and Picric Acid (PA). Although the prepn of PA from phenol is no longer practiced in the USA, it was used as late as WWII in Engl, Fr, Ger, Italy, Japan and the USSR.

Analyses and tests for phenol are given in Ref 1, 134–36, (77) & [135–137]

2-Azidophenol (Phenol azide, o-Hydroxyphenylazoxime, o-Oxydiazobenzolimid). N₃C₆H₄OH, mw 153.12, N 31.10%, OB to CO₂ -159.9%; colorless crystals with 1/3 H₂O from w; mp, darkens and decomps at 120–130⁰; bp, detones violently at 140–150⁰. Sol in alc, AcOH, acet and ethyl acet; difficulty sol in w, chl and petr. Can be prepd by acidifying its Na salt (see below) as described by Forster and Fierz (Refs 1 & 2). It is an expl compd and forms many salts, some of which are expl. For example:

**Sodium Azidophenolate.** N₃C₆H₄ONa, mw 157.11, N 26.75%, OB to CO₂ −132.4%, colorless crystals. Can be prepd by diazotizing o-aminophenol with Na nitrite, adding hydroxylamine hydrochloride, followed by pouring the mix into ice-cooled Na carbonate:

\[
\text{C}_6\text{H}_4(\text{OH})\text{NH}_2 + \text{NaNO}_2 \xrightarrow{\text{HCl}} \text{C}_6\text{H}_4(\text{OH})\text{N}_2\text{OH} + \text{NaHCO}_3
\]

**C₆H₄(OH)N₃**

\[
2\text{C}_6\text{H}_4(\text{OH})\text{N}_3 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{C}_6\text{H}_4(\text{OH})\text{Na} + \text{CO}_2 + \text{H}_2\text{O}
\]

Na azidophenolate expls with considerable violence when heated. The corresponding K salt only chars when treated under similar conditions. The K, Pb and Ag salts were also prepd by Forster and Fierz (Ref 2, 1356–7), but were not investigated from the point of view of their explosibility.

**Refs:** 1) Beil 6, 293–4 2) M.O. Forster & H.E. Fierz, JCS 81, 1352–7 (1907)

**2-Azido-4,6-Dinitrophenol (4,6-Dinitrophenol azide, 1-Hydroxy-4,6-dinitrophenylazide).** (HO)N₃C₆H₄(NO₂)₂, mw 225.12, N 31.11%, OB to CO₂ −60.4%. Certain metallic expls of this compd have been prepared by J.D. McNutt for use in the manuf of primer mixts:

**Lead Dinitroazidophenolate.**

Pb[O·N₃C₆H₄(NO₂)₂]₂. This was prepd by the reaction between dinitroazidophenol, Na azide and Pb nitrate (Refs 1 & 3). By employing this material, McNutt claimed that MF can be eliminated, thus providing non-mercuric priming mixts. Although its impact and friction sensitivity is approx that of MF, smaller percentages of Lead Dinitroazidophenolate than that of MF can be employed because of its lower d and greater ability to propagate flame. Its brisance is between that of MF and Pb Azide, and it is very stable and compatible with most common ingredients of priming mixts suitable for small arms ammo, commercial detonators, artillery ammo, etc. The following examples of priming mixts are given by McNutt (Ref 1): 1) Pb Dinitroazidophenolate (PbDNAzP) 15, Ba nitrate 30, Pb dioxide 25, Sb silicide 18, Ca silicide 6, & Trinitroresorcinc 6%; 2) PbDNAzP 15, Ba nitrate 25, Pb dioxide 12, Diazodinitrophenol 17, Trinitroresorcinc 8, ground glass 22, & gum arabic 1%

The same investigator (Ref 3) proposed the following primer mixts for small arms ammo:

1) PbDNAzP 13, Basic Pb Stypnate 27, double salt of K and Ba nitrate 30, Sb silicide 7, & ground glass 23%; 2) PbDNAzP 8, Basic Pb Stypnate 22, double salt of K and Ba nitrate 40, Sb silicide 23, & Ca silicide 7%

In other primer mixts, McNutt proposed (Ref 2): 1) PbDNAzP 15–20, Ag salt of Tetrazene 7–12, Ba nitrate 17–35, Pb dioxide 10–25, Sb silicide 15–25, & Ca silicide 0–10%; 2) PbDNAzP 15–25, Ag salt of Tetrazene 15–25, Pb dinitroxybenzoic acid 8–15, Ba nitrate 15–25, Pb dioxide 5–10, & ground glass 20–25%

**Refs:** 1) J.D. McNutt, USP 1906394 (1933) & CA 27, 362 (1933) 2) Ibid, USP 1930653 (1933) & CA 28, 328 (1934) 3) Ibid, USP 2002960 (1935) 4) Blatt, OSRD 2014 (1944)

**Potassium Dinitroazidophenolate (called Potassium Dinitrophenylazide by McNutt).** KO₃N₃C₆H₄(NO₂)₂. It was proposed as an ingredient of primer mixts suitable for small srm and artillery ammo, commercial blasting caps, etc. Typical mixts suggested were: 1) K Dinitroazidophenolate 16, Basic Pb Stypnate 15, Ba nitrate 40, & Sb silicide 29%; 2) K Dinitroazidophenolate 17, Basic Pb Stypnate 18, Ba nitrate 35, Pb thiocyanide 5, & ground glass 25%

**Ref:** J.D. McNutt, USP 2005197 (1935) & CA 29, 5274 (1935)

**Sodium Dinitroazidophenolate (called Sodium Dinitrophenylazide by McNutt).** NaO₃N₃C₆H₄(NO₂)₂. Prepd from dinitroazidophenol and Na azide as an intermediate in the prepn of Pb Dinitroazidophenolate, which is obtained on addition of Pb nitrate to the Na salt (see above). No mention is made in the ref about using this salt in expl mixts.
Ref: J.D. McNutt, USP 1930653 (1933) & CA 28, 328 (1934)

Mononitrophenols. \( \text{O}_2\text{N.C}_6\text{H}_4\text{OH}, \) mw 139.11, N 10.07%, OB to \( \text{CO}_2 \) -133.17%. Three isomers are possible but only two (o- and p-) are obtained by direct nitration. The nitration of phenol is much easier than that of aromatic hydrocarbons such as benz or toluene.

Ortho-(or 2-) Mononitrophenol. Yel needles or prisms, mp 44-45°, bp 214-16°, d 1.495g/cc. Prep by the action of dil nitric acid on phenol at low temp; some p-compd is formed at the same time; the o-form is sep'd by steam distn. Si sol in cold w; freely sol in hot w, alc, benz, eth, Cs2 and alkali hydroxides. Highly toxic by ingestion and inhalation. Forms salts, of which the Pb salt expls mildly when heated rapidly (Ref 1, [209])


Meta-(or 3-) Mononitrophenol. Monoclinic prisms from eth or dil HCl; mp 97°; bp 194° at 70mm, decomp when distd at ordinary pressure; d 1.485g/cc at 20°, 1.2797 at 100°. Does not volatilize with steam; cannot be prep'd by the nitrataion of phenol. Can be obtained by boiling diazotized m-nitroaniline with w and sulfuric acid (Ref 3). Si sol in w, sol in alc. Highly toxic by ingestion and inhalation


Para-(or 4-) Mononitrophenol. Yellowish monoclastic crystals; mp 113-14°; bp 279° decomp; d 1.479-1.495 at 20°. Can be prep'd from p-chloronitrobenzene. Sol in hot w, alc & eth. Most toxic of the three isomers by ingestion and inhalation


Commercial Mononitrophenol. Yel cryst mass; mp about 45°; mostly ortho- with some para- nitrophenol. Can be prep'd by the nitration of phenol with dil nitric acid (1:3) at a temp below 35° (see Ref, p 283). Although it does not possess expl properties and does not gelatinize NC, it has been used as the fuel component of some commercial expls. It forms salts, some of which are weak expls which were used in expl comps, for example, Voigt Explosives (qv)

Refs: Colver (1938), 283-4 & 286

Dinitrophenols. \( \text{O}_2\text{N}_2\text{C}_6\text{H}_3\text{OH}, \) mw 184.11, N 15.22%, OB to \( \text{CO}_2 \) -78.30%. Six isomers are possible, and all are expl. The most important one is 2,4-Dinitrophenol, which has been used as a component of various expl mixts. The expl properties of 2,5- and 2,6-Dinitrophenol have also been examined

2,3-Dinitrophenol. Yel needles from w or thick crystals from alc.; mp 144-5°; d 1.681 at 20°. Can be prep'd by the nitration of m-nitrophenol, with 2,5- and 3,4-Dinitrophenols being formed simultaneously. Very easily sol in eth and hot alc

Refs: Beil 6, 251, (125), [239] & (854)

2,4-(or alpha-) Dinitrophenol. Yel orthorhombic crystals from w, leaflets from alc.; mp 112-14°; bp (decomp); d 1.683g/cc at 24°, 1.4829 at 72.5/4°. Sublimes when carefully heated; volatile with steam. Can be prep'd by the nitration of phenol, but this method is not considered commercially practicable because of partial decomp of the phenolic ring. A better method is by hydrolysis under pressure of 2,4-dinitrochlorobenzene, which in turn can be obtained by nitrating chlorobenzene. Other methods are given in Ref 1

Its solubility in various solvents was detd by Desvergnes, RevChimInd 36, 196 (1927), and are given in Ref 1, p [240] in g/100g of solvent at the temps listed:
### Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>15°</th>
<th>34°</th>
<th>34.5°</th>
<th>50°</th>
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<tr>
<td>Ethyl acetate</td>
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<td>–</td>
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<td>–</td>
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<td>–</td>
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<td>–</td>
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<tr>
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<td>–</td>
<td>13.3</td>
</tr>
<tr>
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<td>–</td>
<td>25.7</td>
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<td>–</td>
<td>71.0</td>
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<td>1.8</td>
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<tr>
<td>Toluene</td>
<td>6.4</td>
<td>–</td>
<td>–</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Solubility in water: 12.5°, 0.02; 54.5°, 0.137; 75.8°, 0.301; 87.4°, 0.587; 96.2°, 1.22; 100°, 1.32

2,4-Dinitrotoluene is a highly toxic material, and is readily absorbed thru intact skin. Vapors are absorbed thru the respiratory tract. It produces a marked increase in metabolism and temp. profuse sweating, collapse and death. It can also cause dermatitis, cataracts, wt loss, granulocytepenia, polineuropathy, and exfoliative dermatitis (Ref 10)

Commercial Dinitrophenol consists almost entirely of 2,4-Dinitrophenol, and its properties are identical with those given above

2,4-Dinitrophenol is an exp less powerful and brisker, and less sensitive to mechanical action than TNT, but more sensitive than DNB or DNT. Some of its exps were detd in Ger by Will (Ref 2) and Wöhler (Ref 4), in Fr by Burtot (Ref 6), and in the USA by the Ordnance Dept (Ref 9):

**Brisance (by Sand Test).** A 0.4g sample, using an MF detonator, crushed 23g of sand vs 43g for TNT

**Impact Sensitivity.** PicArsn app with 2kg wt, 17° vs 14° for TNT

**Explosion temp.** About 315°

**Q<sub>E</sub>** = 647.6cal/mole

**Power (by BalMort).** 70% of TNT

**Rifle bullet test.** No detonations from impact of .30 cal bullets fired from a distance of 90 ft

**Reaction with metals.** Forms salts except with Al and Sn

**Thermal stability.** Satisfactory

**Velocity of detonation.** About 5000m/sec vs 6900 for TNT

Uses. 2,4-Dinitrophenol has not been used alone as a shell filler because of its high mp (it would require press loading), and because it is comparatively expensive to manuf. When added in quantities of up to 40% to Pa, it lowers its mp sufficiently to permit cast loading. Such mixts were known as Tridites in the USA, as Shellite (PA 70/2,4-DNPh 30) in Eng, as DD Explosifs (see Vol 3, D19-L) in Fr, and as MBT (PA 60/2,4-DNPh 40) in Italy. These mixts were used for loading bombs and shells

### Salts of 2,4-Dinitrophenol

2,4-DNPh forms numerous metallic salts, most of which are exp, eg:

- **Ammonium salt.** NH₄C₆H₃O₄N₂.H₂O, yel needles, mp about 220° with partial sublimation; sl sol in w and alc; expl (Ref 5, 290)

- **Barium salt.** Ba(C₆H₃O₄N₂)₂·4H₂O, golden-yellow crystals, sol in hot w or 90% alc (Ref 1, 253)

- **Cobalt salt.** Co(C₆H₃O₄N₂)₃·4H₂O, orange-red prisms from alc; loses 3CoCl₂.H₂O at 95°; expls on heating on a Pt foil (Ref 1, 241)

- **Lead salt (basic).** (O₂N₂)C₂H₃O₂·3Pb(OH)₂H₂O, yel spears; mp, expls violently when heated; d 2.817g/cc at 20/20°, sl sol in hot w (Ref 1)

- **Lead salt (neutral).** [(O₂N₂)C₂H₃O₂]·3Pb·6H₂O; orange-yel powder, which is, according to Colver, one of the most violently detonating expls (Ref 5, 290)

- **Potassium salt.** KC₆H₃O₄N₂·H₂O, yel prisms, d 1.778g/cc at 20°, expl (Ref 1, 253)

- **Silver salt.** AgC₆H₃O₄N₂·H₂O, needles, d 2.755g/cc at 20°, expls violently when heated (Ref 1, 253)

- **Sodium salt.** NaC₆H₃O₄N₂·H₂O, pale yel needles, sol in w, expl (Ref 1, 253; Ref 5, 290)

### Additive Compounds of 2,4-Dinitrophenol

2,4-DNPh forms low mp additive compts with ammonia or amines (aniline, toluidine, naphthylamine, etc.), which on intimate mixing with oxidants (AN, K nitrate, Na nitrate, K chlorate, K perchlorate, etc) form easily detonable expls. Colver (Ref 5, 291) describes preparative methods and gives mp's of some of the additive compts. For example, 2,4-DNPh (mp 112–14°) combines with aniline to form an additive compd of mp 82° [See also Gerp 72945 (1893) & 73205 (1893), described in Ber 27 (Referate), 356–7 (1894)].

Refs: 1) Beil 6, 251–54, (125–26), [239–42], & (854) 2) W. Will, SS 1, 212 (1906)
3.4-Dinitrophenol (d-Dinitrophenol). Colorless, shiny crystals; mp 134–35° (when in w, it melts at 50–60° and remains liq for a long time); d 1.672g/cc; heat of fusion 6.05 kcal/mole. It is formed, together with 2,3- and 2,5-Dinitrophenol, on nitration of 3-nitrophenol. It does not volatilize with steam, is sl sol in hot w, v sol in alc and ether. Its expl props have not been examined
Refs: 1) Beil 6, 257, (127), [246] & [868]
2) A.F. Holleman & G. Wilhelmy, Rec 21, 434 (1902)

3.5-Dinitrophenol (e-Dinitrophenol). Colorless leaflets from w; mp 126.1°; d 1.702g/cc. Can be prep’d by heating 3,5-dinitroanisole in a sealed tube with conc HCl at 170–80° for 5–6 hrs, or by other methods. Very sol in alc or eth, sol in chlor or benz, sl sol in w or petr eth. Its expl props have not been examined
Refs: 1) Beil 6, 258, (128), [246] & [869]
2) A.F. Holleman & G. Wilhelmy, Rec 21, 438 (1902)

Trinitrophenols. \((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\cdot\text{OH}\), mw 229.11, N 18.3%, OB to CO\(_2\) 45.3%. Several isomers are known, all of them expl:

2.3,5-Trinitrophenol (γ-Trinitrophenol). Yel needles from w, mp 118°. Can be prep’d by the nitration of 2,3-Dinitrophenol or by other methods. Very sol in alc, eth and benz; sol in hot w, diff sol in cold w. It is an expl; forms metallic salts such as those of K, Ba, Ag and Pb
3) J.J. Blanksm, Rec 21, 258 (1902)
4) Urbański 1, 524 (1964)

2.4,5-Trinitrophenol (β-Trinitrophenol). White needles from dil alc, mp 96°. Can be prep’d by the nitration of 3,4-Dinitrophenol or by other methods. Very sol in alc, eth and benz, sol in hot w, diff sol in cold w. It is an expl; forms metallic salts such as those of K and Ba
2,4,6-Trinitrophenol (α-Trinitrophenol). See under Picric Acid

2,4,6-Trinitrophenol, Ammonium Salt. See under Ammonium Picrate (Explosive D) in this Vol

Trinitrophenols, Halogen Derivatives of.

Several more or less expl halogen comps of Trinitrophenols are listed in Beilstein, ie:
3-Chloro-2,4,6-Trinitrophenol.
(O₂N)₃C₆H(OH)Cl, crspts, mp 112.5°–113.5° (Beil 6, [283])
3-Chloro-2,4,6-Trinitrophenol. Yel crspts, mp 112–116° (Beil 6, 292 & [283])
3,5-Dichloro-2,4,6-Trinitrophenol.
(O₂N)₃C₆(OH)Cl₂, colorl crspts, mp 135–40° (Beil 6, 292 & [141])
3-Bromo-2,4,6-Trinitrophenol.
(O₂N)₃C₆H(OH)Br, yel crspts, mp 144–49° (Beil 6, 292 & [283])
3,5-Dibromo-2,4,6-Trinitrophenol.
(O₂N)₃C₆(OH)Br₂, crspts, mp 146° (Beil 6, [283])
3,5-Dibromo-2,4,6-Trinitrophenol.
(O₂N)₃C₆(OH)Br₂, colorl crspts, mp 173° (Beil 6, 292 & [283])
5-Chloro-3-bromo-2,4,6-Trinitrophenol.
Br(O₂N)₃C₆H(OH)Cl, pale yel prisms, mp 165.5° (Beil 6, [283])
3-Iodo-2,4,6-Trinitrophenol.
(O₂N)₃C₆H(OH)I, crspts, mp 197° (Beil 6, [283])

2,3,4,6-Tetranitrophenol. (O₂N)₄C₆H₂OH, mw 274.10, N 20.44%, OB to CO₂ –23.3%, light yel needles from chl, mp 140° (decomps at higher temps). Sol in alc, chlfd and ethyl acetate; diff sol in benz or lig.

It was first prepd by Nietzki and Burckhardt (Ref 2) by the action of 50% nitric acid followed by 63% nitric acid on diquinoyltriioxime, C₆H₂(ONO)₂(NO)₃ (Beil 7, 886), at a temp lower than room temp. By neutralizing the soln, a sparingly sol K salt was pptd, which in turn was converted by double decomps into a still less sol Ba salt. From the latter, by the action of a calcd qty of sulfuric acid, free Tetranitrophenol was obtained

A product of higher purity than that obtained by Nietzki was prepd by Blanksma (Ref 3) by the nitrtn of m-nitrophenol with a mixt of nitric acid (d 1.52g/cc) and concd sulfuric acid. As shown later (Ref 4), the product, if of high purity, exhibits fairly high heat stability. It expls at 245–251°, whereas if it is contaminated it decomps after being brought to its mp (140°)

Its expl props were incompletely examined by van Duin and van Lennep (Ref 4). They reported an expln temp of 251° when heated at 20° per minute; 245° when heated at 5° per minute. Its impact sensitivity was less than PETN and more sensitive than Tetryl, and it evolved nitrous gases after being heated at 70° for 4 hours

Refs: 1) Beil 6, 292, (141), [284] & [73]  
2) R. Nietzki & E. Burckhardt, Ber 30, 175 (1897)  
3) J.J. Blanksma, Rec 21, 256 & 336 (1902); Ibid Ber 47, 687 (1914)  
4) C.F. van Duin & B.C.R. van Lennep, Rec 39, 145, 162, 166, 170 & 174 (1920)  
5) Urbanński 1 (1964), 530–1

Tetranitrophenol, Halogen Compounds of.

5-Chloro-2,3,4,6-Tetranitrophenol.
(O₂N)₄C₆H(OH)Cl, colorl crspts from chlfd or C tetrachloride, mp 174°. Can be prepd by the nitrtn of 5-chloro-3-nitrophenol with mixed nitric-sulfuric acids. It is an expl

5-Bromo-2,3,4,6-Tetranitrophenol.
(O₂N)₄C₆H(OH)Br, colorl crspts from chlfd or C tetrachloride, mp 157°. Can be prepd by the nitrtn of 5-bromo-3-nitrophenol with mixed nitric-sulfuric acids. It is an expl

Ref: Beil 6, 293

Pentanitrophenol. (O₂N)₅C₆OH, mw 319.12, N 21.95%, OB to CO₂ –7.52%, yel crspts from chlfd, mp 190° (decomp). Was prepd by Blanksma (Ref 2), who nitrated 3,5-dinitrophenol with an anhydr mixt of nitric-sulfuric acids. The product was pptd and recrystd from chlfd. It is a powerful expl

Refs: 1) Beil 6, 293 & [284]  
2) J.J. Blanksma, Rec 21, 256 & 336 (1902)

Nitrosophenols. HO.C₆H₄.NO, mw 123.11, N 11.38%, OB to CO₂ –162.5%
o-Nitrosophenol (1,2-Benzquinone Monoxide). Oil. Can be prepd in 20% yield by treating a hot aq soln of o-nitrosanisole with a boiling K disulfate soln, or by other methods. It expids on heating or in contact with concd acids (Ref 2). It forms expd Ag, Cu and Na salts

Reps: 1) Beil 7, 600, (337) & [566] 2) A. Baeyer & E. Knorr, Ber 35, 3037 (1902) 3) O. Baudisch & N. Karzew, Ber 45, 1164–71 (1912)

p-Nitrosophenol (1,4-Benzquinone Monoxide). Pale yel orthorhombic needles: mp, browns at 126°, decomp at 144°. Can be prepd from phenol by the action of nitrous acid in the cold. Moderately sol in w, sol in dil alkalies giving green to brownish green solns; sol in alc, ether & acet. Q<sub>Q</sub> 713.9 kcal/mole

p-Nitrosophenol expds on contact with concd acid, alkali or fire. A technical grade expd on storage (Ref 4). According to Kuznetzov (Ref 6), its exothermic decompn, often resulting in spontaneous ignition, is caused chiefly by contaminating alkalies. A more stable product can be obtained by washing with dil HCl followed by w. By converting p-Nitrosophenol into its Na salt and drying it at 70°, Kuznetzov obtained a product which could be stored indefinitely at room temp. It changed very little when heated at 130°


**Phenolsulfonic Acids and Derivatives**

HO.C<sub>6</sub>H<sub>4</sub>.SO<sub>3</sub>H, mw 174.17. Three of these acids are known, o-, m-, and p-, but only two of them, o- and p- acids form during the sulfonation of phenol in the manuf of PA by the phenolic process. The formation of small quantities of the m-acid was reported, but not definitely proven

o-Phenolsulfonic Acid. Crysts with 3H<sub>2</sub>O; mp, begins to melt at 50° and then decomp; can be prepd by the sulfonation of phenol

Reps: Beil 11, 234, (53) & [131]

m-Phenolsulfonic Acid. Crysts with 2H<sub>2</sub>O; mp, loses 1.5H<sub>2</sub>O at 100° and the remainder at 140°; can be prepd by diazotizing metaanic acid, H<sub>2</sub>N.C<sub>6</sub>H<sub>4</sub>.SO<sub>3</sub>H, or by other methods

Reps: Beil 11, 239, (54) & [133]

p-Phenolsulfonic Acid. Deliq needles; can be prepd by the sulfonation of phenol or by other methods


**Mononitrophenolsulfonic Acids.**

O<sub>2</sub>N.C<sub>6</sub>H<sub>4</sub>(OH).SO<sub>3</sub>H, mw 273.22. Several acids are described in Beilstein, of which only the o- and p- are formed as intermediate products in the manuf of PA from phenol

o- (1,4,2-) Nitrophenolsulfonic Acid. Crysts with 3H<sub>2</sub>O; mp, loses H<sub>2</sub>O at 100° and then decomp at about 110°; can be prepd by treating 4-nitrophenol with concd sulfuric acid


p- (1,3,4-) Nitrophenolsulfonic Acid. Plates from ethyl acet/ benz; mp 141–2°, its trihydrate melts at 49°; can be prepd by treating 2-nitrophenol with fuming sulfuric acid; v sol in w, ethyl acet, alc and hot chlf


**Sodium Salt of Nitrophenolsulfonic Acid.**

O<sub>2</sub>N.C<sub>6</sub>H<sub>4</sub>(OH).SO<sub>3</sub>Na, mw 241.16, N 5.8%, orange-red crystals. Can be prepd by treating the product obtained on sulfonation of phenol with Na nitrate and an excess of sulfuric acid. This salt, which is a mixt of Na o- and p-nitrophenol- sulfonates, was patented in 1911 by A. Voight for use in expl mixts such as: Na nitrophenolsulfonate 22.5 to 25, K or Na nitrate 45 to 65, K perchlorate 10 to 22.5, and AN 10%

The Vereinigten Köln-Rottweiler Fabriken patented in 1910 its use in the manuf of detonating expls, eg, Na nitrophenolsulfonate (or Na nitroresolsulfonate) 25, Na nitrate 25, and K perchlorate 50%

Reps: Colver (1938), 284–6 & 351

**Dinitrophenolsulfonic Acids.**

(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OH)SO<sub>3</sub>H, mw 264.18, N 10.60%
4,6-Dinitrophenolsulfonic Acid [(4,6-Dinitro-phenolsulfonsäure) in Ger]. Yellowish crystals. It is obtained during the prep of PA by the sulfonation and nitration of phenol. Forms various metallic salts, such as those of Ba and K (Ref 3).


2,6-Dinitrophenolsulfonic Acid (2,6-Dinitrophenolsulfonsäure) in Ger). Yellowish crystals; mp, with 3H₂O, about 111°; can be prepd by the nitration of p-phenolsulfonic acid. Forms numerous metallic salts.

Refs: 1) Beil 11, 247, (57) & (138) 2) M. Marqueyrol & P. Loriette, Bull Fr [4], 25, 371 (1919)

2,6-Trinitrophenolsulfonic Acid [2,4,6-Trinitrophenolsulfonsäure] in Ger] (O₂N)₂C₆H₄(OH)-SO₃H, mw 309.18, N 13.59%, crystals; can be prepd by heating m-phenolsulfonic acid with concd nitric acid; sol in w. Forms expln metallic salts, such as:

- Potassium salt. KC₆H₂N₃O₁₀S.H₂O, orange-red crystals, sol in w
- Barium salt. Ba(C₆H₂N₃O₁₀S)₂.3H₂O, yel prisms, sol in w

Both salts expld violently when heated on a Pt foil

Refs: 1) Beil 11, 240 2) A. Berndsen, Ann 177, 97 (1875)

5-Bromo-3,4,6-Trinitrophenolsulfonic Acid. (O₂N)₂C₆Br(OH)SO₃H, can be prepd by nitrating 3-bromophenol with mixed nitric-sulfuric acid. Its Potassium salt, K₂C₆O₁₄N₃Br₅, yel crystals from alc, expls on heating.

Refs: 1) Beil 11, (132) 2) H.H. Hodgson & F.H. Moore, JCS 1926, 161

Phenothiazine (Thiodiphenylamine, Dibenzotiazine, Phenoxur, Contraverm). C₁₅H₁₄NS, mw 199.26; yel rhomb leaflets or diamond-shaped plates from toluene or butanol; mp 185.1°; bp 371° (760mm), 290° (40 mm), subl at 1mm Hg at 130°. Can be prepd by reaction of diphenylamine and S in the presence of an oxidizing catalyst. Sol in benz & eth, insol in petr eth, chl & w. Moderately toxic by ingestion; a skin irritant. Can be nitrated to form a tetranitroderivative which is expl (Refs 1, 3, 6, 7 & 8)

1,3,5,7-Tetranitrophenothiazine (Phenothiazine Tetranitrosulfoxide). Yel solid, mp 368°. Can be prepd in 70% yield by the nitration of phenothiazine with a mixt of 98% nitric acid and anhyd sulfuric acid at 60°.

In addition to nitrination, oxidation of the S atom also takes place, resulting in the formation of the sulfoxide (Ref 5). It was used in Ger during WWII as a component of a non-fusible expl compn known under the name of “Pressling” (qv) (Ref 2 & 4)


β-Phenoxyethanol and Derivatives

β-Phenoxyethanol (Phenyetheneglycolether, Glycol monophenylether). C₆H₅O.CH₂CH₂OH, mw 138.16; colorless liq with faint aromatic odor, fr p 14°; bp 240-48°; d 1.094 at 20/20°; Rtl 1.534 at 20°; vap press 0.03mm at 20°; sol in w, sol in alc & eth. Can be prepd by heating phenol and ethylene oxide in a closed tube at 150°. It can be nitrated to obtain the expls β-(2,4-Dinitrophenoxy) ethanol Nitrate and β-(2,4,6-Trinitrophenoxy) ethanol Nitrate (see below)

β-(2,4-Dinitrophenoxy) ethanol (Glycaldinitrophenylether). \((O_2N)_2C_6H_5.O.CH_2.CH_2.OH\), mw 228.18, N 12.27%, wh needles, mp 111.3-111.4°, d (apparent) 0.5 g/cc. It was first prep by Fairburne and Toms (Ref 2) by heating a glycolic soln of Na hydroxide with a glycolic soln of dinitrochlorobenzene at 100°. Practically the same method was used by other investigators. Its industrial prep was patented by duPont and others. Wasmér (Ref 4, p 176) gives its properties, including solubility in various solvents at 20°. By nitration it, the expl β-(2,4,6-Trinitrophenoxy) ethanol Nitrate (see below) is obtained

Refs: 1) Beil—not found 2) A. Fairburne & H. Toms, JCS 119, 2207 (1921) 3) C. Dosios & Tsatsas, CR 180, 1275 (1925) 4) A. Wasmér, MP 28, 171 (1938) & CA 33, 8405 (1939) 5) H. Ficheroule, MP 30, 123 (1948) & CA 45, 10586 (1951)

β-(2,4-Dinitrophenoxy) ethanol Nitrate (Glycaldinitrophenylether Nitrate, Dinitrophenylglycol-ether Nitrate). \((O_2N)_2C_6H_5.O.CH_2.CH_2(ONO_2)\), mw 273.16, N 15.38%, OB to CO₂ -67.4%, crs, mp 64-67°, Qₕ 3455 cal/g, Qᵣ 181 cal/g (Ref 5)

It can be prep from dichlorobenzene and ethylene glycol, followed by nitrilation of the resulting glycol monophenyl ether. It is an expl, slightly less powerful than TNT (Trauzl block expansion gave 270-277cc vs 290-294cc for TNT), and very insensitive to impact (using the Kast app with a 2kg wt, it detonated at > 120cm vs > 40cm for TNT). It was proposed for use in propellants, primers or detonators (Ref 6)


β-(2,4,6-Trinitrophenoxy) ethanol Nitrate (2,4,6-Trinitrophenoxethyl Nitrate, Glycoltrinitrophenylether Nitrate, TNPEN).\((O_2N)_3C_6H_2.O.CH_2.CH_2(ONO_2)\), mw 318.16,

N 17.61%, OB to CO₂ -45.3%, light yel crs, mp 104.5-107°, Qₕ 1291 kcal/mole, Qᵣ 66.7 kcal/mole. Schmidt (SS 29, 263 (1934)) gives Qᵣ as 897.7 kcal/mole

TNPEN was first prep by Lewis (Ref 2), and subsequently by several other investigators (see Refs 3, 4, 5 & 7). Ficheroule (Ref 7) prep it in 1937 at the Laboratoire Central des Poudres, by the nitration of β-(2,4-Dinitrophenoxy) ethanol, but the results were not published until 1948 (Ref 3). The substance was purified by pptn of the nitrated mixt with w, and crysfn from acet

Wasmér (Ref 4) investigated several methods proposed prior to 1938, and developed his own method, which he describes in detail

Elderfield (Ref 5) gives the following method of prep: “A solution of 10g of β-(2,4-Dinitrophenoxy) ethanol in 100g of 94% sulfuric acid was added slowly and with stirring to 75g of mixed acid (52.7% sulfuric, 26.5% nitric and 21% water) at 0-10°. Since the reaction is distinctly exothermic, an ice-salt bath was necessary for cooling. When the addition was complete, the temp was raised in 1/2 hour intervals to 20°, 30°, 40°, 60°, and then in 1/4 hour intervals to 70°. After chilling, the cream-colored crs were filtered on sintered glass, washed free of acid and recrystd by dissolving in acet and adding alc”

TNPEN ignites when heated in an open dish and expls when struck with a hammer upon an iron surface. It is a good gelatinizer for NC. Properties: According to Wasmér (Ref 4): Solubility. At 20° in g/100ml of solvent; acet 27.7; benz 2.1; chlf 0.6; eth 0.3; CS₂ 0.06; CCl₄ 0.03; w <0.1; concd sulfuric acid, sl sol; concd nitric acid, sol

C.U.P. (Trauzl block value), 109 (PA 100) Impact sensitivity. Between that of PA and Tetryl Stability. Bergmann-Junk test at 132°; one g of the pure product, mp 104.5°, evolved between 0.3 and 1.7 cc of NO; the impure (crude) material, mp 102-102.5°, deflagrated

It was found to be a good gelatinizer for NC, and for this reason was recommended as an ingredient of smokeless powders

According to WASAG (Ref 3): Impact sensitivity. 2kg wt, positive at > 45cm vs > 40cm for TNT, ie, comparable to TNT Power. (Trauzl test). 122% of TNT
According to Fichereolle (Ref 7):  
*C.L.P.* (Traufl block value), 115 (PA 100, Tetryl 120)  
Gap test. 23cm vs 22cm for Tetryl  
Impact sensitivity. 5kg wt; 50% explns obtained with a fall of 80cm; comparable to Tetryl  
Sensitivity to initiation. Comparable to that of Tetryl  
Detonation velocity at various densities and pressures.  

\[
\begin{array}{cccc}
\text{Density, g/cc} & \text{P*} & \text{VD**} & \text{P} & \text{VD} \\
1.15 & 75 & 5500 & 40 & 5638 \\
1.25 & 100 & 6100 & 100 & 6100 \\
1.35 & 175 & 6606 & 175 & 6602 \\
1.40 & 200 & 6856 & 225 & 6777 \\
1.45 & 300 & 6700 & - & - \\
1.50 & 400 & 6600 & 360 & 7137 \\
1.60 & - & - & 450 & 7240 \\
\end{array}
\]

*P = Press in kg/sq cm necessary to obtain desired d  
**VD = Detonation velocity (mean) in m/sec

**Uses:** Lewis (Ref 2) recommended the use of TNPEN in boosters and detonators, while WASAG (Ref 3) advocated its utilization as an addition to propellants as well as in the manufacture of primers and detonators.  
WASAG also prep'd and tested the following formulation: TNPEN 64, Pentaerythritol dimethyl etherdinitrate 18, and Al powder 18%. It had a mp 94°C; impact test value with a 5kg wt, max height (29cm) with no expln vs 20cm for PA; Traufl block value 440cm² vs 310cm² for PA (10g sample)  
Both Wasmer (Ref 4) and Fichereolle (Ref 7) employed TNPEN as an ingredient in smokeless powders (poudres SD)  
Lang (Ref 8) investigated mixes of TNPEN with AN, and noted that they were more hygroscopic than AN alone. These mixes were fairly stable at room temp, but when heated to 115°C, they combined in equimolecular proportions, forming a complex more volatile than either of the constituents  

**Refs:**  
1) Beil—not found  
2) H.A. Lewis, USP 1560426 (1925) & CA 20, 112 (1926)  
3) Westfälisch-Anhaltische Sprengstoff AG (WASAG), GerP 551306 (1931) & CA 26, 4474 (1932); GerP 572937 (1933) & CA 27, 4402  
4) A. Wasmer, MP 28, 177 (1938) & CA 33, 8405 (1939)  
5) R.C. Elderfield, "Explosives from Hydroxy and Amino Compounds", ORSD 907 or PB 13085 (1942)  
6) Davis (1943), 227  
7) H. Fichereolle, MP 30, 128–129 (1948) & CA 45, 10586 (1951)  
8) F.M. Lang, MP 34, 189–94 (1952)  
9) L. Médard & M. Thomas, MP 35, 159 & 172 (1953)

**Phenylaminobutane.** See N-Butylaniline and Derivatives in Vol 2, B378-L ff

**Phenylaminobutanol (Phenylaminobutyl alcohol).** See Anilinobutanol and Derivatives in Vol 1, A422-R

**Phenylamoethane.** See N-Ethylaniline and Derivatives in Vol 6, E206-L

**Phenylaminoethanol (Phenylaminoethyl alcohol).** See Anilinoethanol and Derivatives in Vol 1, A424-L ff

**Phenylaminomethane.** See N-Methylaniline and Derivatives in this Vol, M97-R ff

**Phenylaminopropanediol.** See Anilinopropanediol and Derivatives in Vol 1, A434-R

**Phenylaminopropanol.** See Anilinopropanol and Derivatives in Vol 1, A436-L

**Phenylaniline.** See Aminobiphenyls and Derivatives in Vol 1, A191-L

**Phenylarsonic Acid (Phenylarsinic Acid).**  
C₆H₅AsO(OH)₂, mw 202.03, crsfts, mp 157–8°C  
loses H₂O > 158°C, d 1.760g/cc. Prepn and properties are given in Ref 1
Lead-2,4,6-trinitrophenylarsonate.  
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_3\text{As}((\text{O}_2\text{Pb}), m w 542.23, N 7.75\%, ochre-colored solid, mp 215\text{-}237^\circ\). Can be prepd by treating K trinitrophenylarsonate,  
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_3\text{As}((\text{OK})_2\) (obtained by the reaction between 2,4,6-trinitrobenzoyl chloride and \(K\) arsenite) with \(\text{Pb}\) acetate.

It is an expl, comparable in sensitivity to Tetryl and about 51\% as powerful as TNT (by Balmont test); expls when heated to 270\%. It is rather volatile and hygroscopic, but fairly stable even at temps as high as 135\%.

Refs: 1) Bell 16, 868, (448) & [457]  
2) R. McGill, OSRD 830 (1942), 36

Phenylazide and its Nitrated Derivatives. See under Azido and Azidonitro Derivatives of Benzene in Vol 2, B42-L ff

Phenylazoanilines. See under Aminobenzene and Derivatives in Vol 1, A184-R to A185-L

Phenylbenzoic Acid. See Biphenylcarboxylic Acid and Derivatives in Vol 2, B125-L

Phenyl Cyanide. See Benzonitrile and Derivatives in Vol 2, B76-R

Phenyldiazosulfide [Di(Benzenediaz) Sulfide].  
C\(_6\)H\(_5\)N\(_2\)S\(_2\), m w 242.27, N 23.13\%, red solid. It was prepd at PicArsn in quantities of 0.5 to 1.0g by diazotizing aniline, and either passing hydrogen sulfide thru the diazochloride soln or adding Na sulfide to it at 0\%. It pptd in the form of a yel colloid which slowly agglomerated to produce a red solid which floated on the surface. The red solid turned to an oil in a short time when the soln was allowed to warm to room temp, and during the change nitrogen was evolved and the odor of thiophenol was apparent. The wet material expld easily under the action of friction, impact, or heat from a match flame. When removed from soln, pressed dry on filter paper, and air dried at room temp, the compd detonated spontaneously

p-Nitrophenyldiazosulfide.  
\((\text{O}_2\text{N})\text{C}_6\text{H}_4\text{N}=(\text{N})\text{N}=(\text{N})\text{C}_6\text{H}_4(\text{NO}_2), m w 332.27, N 25.30\%\), fine yel crys. It was prepd at PicArsn by diazotizing p-nitroaniline, neutralizing the mixt, and either passing hydrogen sulfide thru the soln or adding Na sulfide to it at 0\%. It is more stable than Phenylidiazosulfide, and is difficult to expld when wet. It can be dried without change at room temp, but the resulting dry compd is extremely sensitive to friction; it can be detonated by rubbing on smooth linoleum with a soft object.

p-Nitrophenyldiazosulfide is readily decomd by org solvents at room temp with the evolution of nitrogen. It expld at 82\% in 5 seconds (vs 335\% for LA, 260\% for Tetryl and 208\% for MF); impact sensitivity with a 500g wt on the BuMines app, 5cm fall for expln vs 65cm for commercial LA.

Refs: 1) E. Bamberger & J. Kraus, Ber 29 (1), 272–86 (1896)  
2) W.R. Tomlinson, PATR 1208 (1942)  
3) Ibid, C&EN 29, 5473 (1951) & CA 46, 3279 (1952)

Phenyl dichloramine (N,N-Dichloraniline).  
C\(_6\)H\(_5\)NCl\(_2\), m w 162.02, yel-red oil. It was prepd by Goldschmidt (Ref 2) by action of hypochlorous acid on aniline in ethereal soln at -15\% to 20\%. Sol in eth; the soln is fairly stable when kept at 0\% and in the dark. The oil alone is stable at -40\%, but expls at higher temps. It also expls on contact with concd sulfuric acid.

Refs: 1) Bell 12, (287)  
2) S. Goldschmidt, Ber 46, 273 (1913)  
3) Sidgwick, ChemElemns 1 (1950), 708

**PHENYLENEDIAMINES OR DIAMINOBENZENES**

H\(_2\)N\(_2\)C\(_6\)H\(_4\)NH\(_2\), m w 108.14, N 25.91\%. There are three isomers; ortho-, meta- and para.
Phenylenediamines were first prepd in the 1860's by P. Griess and then by A.W. Hofmann. Inasmuch as some confusion existed in regard to the structure of these compds, it is difficult to say which isomers they were
o- or 2-Phenylendiamine (1,2-Diaminobenzene). Colorless monocryls, darkens in air; mp 102–104°; bp 252–258°; sol in alc, eth, w & chlf; somewhat toxic. Can be prep'd by reducing o-nitroaniline with Zn and NaOH; many other methods are known (Ref 1).

Forms numerous salts as well as additive compds, some of which are expl

Salts and Additive Compounds.
Perchlorate. C₆H₅N₂+2HClO₄; mw 309.16; N 9.1%; OB to CO₂, Cl₂ & H₂O −46.6%; crysts; explds at 250° (Ref 1, p 6 & Ref 3).

With Zn Perchlorate. C₆H₅N₂+ZnClO₄; prisms; difficultly sol in w; puffs off on heating (Ref 1, p 11 & Ref 4).


m- or 3-Phenylendiamine (1,3-Diaminobenzene). Colorless needles, unstable in air; usually in the form of the stable hydrochloride; mp 63°, bp 282–287°, d 1.13899 gc/cc. Sol in alc, eth & w. Can be prep'd by the reduction of m-nitrobenzene or nitroaniline with Fe and hydrochloric acid. It is a strong skin irritant. Forms salts and additive compds, some of which are expl.

Salts and Additive Compounds.
Monoperchlorate. C₆H₅N₂+HClO₄; colorless crysts; can be prep'd by treating m-phenylenediamine with perchloric acid. Explnds when heated to about 250°, or on impact. It is less sensitive to mechanical action than the diperchlorate.

Diperchlorate. mw 309.16, N 9.1%, OB to CO₂, Cl₂ & H₂O −46.5%; yel crysts; mp, expls at about 263°. Can be prep'd by treating m-phenylenediamine with perchloric acid. It is fairly sol in w, v sol in alc, sol in acet & eth with decomp, difficulty sol in acet ac, insol in chlfr. Stable toward light.

The expl propeties of the diperchlorate were examined in 1917 by Spallino (Ref 1, p (11)), and then by Datta & Chatterjee (Ref 2). It expls on heating, impact or friction. Its power and brisance are slightly below those of PA, while sensitivity to mechanical action is much higher (for example, the impact test with a 2kg wt is only 15cm vs 85cm for PA). When ignited, it burns rapidly with sooty smoke (Ref 1, p (11)).

With 1,3,5-Trinitrobenzene.
C₆H₅N₂+2C₆H₅NO₃; mp 168°; was prep'd by Kremann et al (Ref 3). There are also eutectics; at 45° with m-phenylenediamine 82, TNB 8%; and at 105° with m-phenylenediamine 7, TNB 93% (Ref 1, p [24]).

With 2,4,6-Trinitrotoluene.
C₆H₅N₂+C₆H₅NO₃; mp 105°; was prep'd by Kremann et al (Ref 3). There are also eutectics; at 57.5° with m-phenylenediamine 90.5, TTN 9.5%; and at 70° with m-phenylenediamine 6, TTN 94% (Ref 1, p [24]).

Refers: 1) Bell 13, 33, (10–11) & [23]

p- or 4-Phenylendiamine (1,4-Diaminobenzene). White to light purple crystals, oxidizes on standing in air to purple and black; mp 145–147°; bp 267°; sol in w & chlfr; easily sol in alc & eth; affected by light; flash pt 155.5°; combustible.

Can be prep'd by reduction of p-nitroaniline with Fe and hydrochloric acid; other methods given in Ref 1. It is highly toxic by ingestion and inhalation; strong irritant to the skin. Tolerance, 0.1 mg per cubic meter of air.

It forms salts and additive compds, some of which are expl.

Salts and Additive Compounds.
Perchlorate. C₆H₅N₂+2HClO₄; mw 309.16, N 9.1%; OB to CO₂, Cl₂ & H₂O −46.6%; yel to brownish leaflets; mp, expls at about 260°; very easily sol in w, difficulty sol in ac, insol in eth. Expls on heating or on impact.

Was prep'd and examined by Spallino (Ref 1, p (20)) and Datta et al (Ref 2). Its sensitivity to impact (60cm with a 2kg wt) is much lower than the corresponding orthocomp (15cm with a 2kg wt). When ignited in air, it burns rapidly with the production of a sooty flame.

p-Phenylenediamine-picrate.
H₃NC₆H₄N₂H₃C₆H₅(OH)(NO₂)₃, mw 337.25, N 20.8%. Can be prep'd by mixing equimolar quantities of PA and p-phenylenediamine dis-
solved in alc or other solvent. Kaiser (Ref 4) proposed that it be used in combination with diazodinitrophenol in percussion caps p-Phenylenediamine-dipicrate. H₂NCC₆H₄NH₂·[C₆H₄(OH)(ONO₂)₃]₂, mw 566.36. Can be prep'd by the interaction of 1 mole of p-phenylenediamine with 2 moles of PA in alc or other solvent. It was patented by J. Piccard (Ref 5) for use in delay electric caps for igniting time fuses, etc.

**Compound with 1,3,5-Trinitrobenzene.**
C₆H₅N₂+C₆H₃(NO₂)₃, mp 145.5°. Was prep'd by Kremann & Mauermann (Ref 3). There are also eutectics; at 101–5° with p-phenylenediamine 9, TNB 91%; and at 116° with p-phenylenediamine 64, TNB 36% (Ref 1, p 70 & [37]).

**Compound with 2,4,6-Trinitrotoluene.**
C₆H₅N₂+C₇H₃(NO₂)₃, mp 93°. There are also eutectics at 64° with p-phenylenediamine 8, TNB 92%, as well as at 88° with p-phenylenediamine 64, TNT 36%


**Nitrophenylenediamines or Nitrodiaminobenzenes**

Mono-, di-, and tri-nitrophenylenediamines are described in the literature (Ref 1), but no tetra-compd. The 2,4,6-Trinitro-m-phenylenediamine is an expl

**2,4,6-Trinitro-m-phenylenediamine** (2,4,6-Trinitro-1,3-dianinobenzene, 2,4,6-Trinitrophenylenaminodiamino (1,3) in Ger, 2,4,6-Trinitrometaphenylenediamin

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Maximum Fall for 0/6 Shots</th>
<th>Minimum Fall for 6/6 Shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,6-Trinitro-m-phenylenediamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetryl</td>
<td>51 cm</td>
<td>14 cm</td>
</tr>
<tr>
<td>TNT</td>
<td>&gt; 60 cm</td>
<td>&gt; 24 cm</td>
</tr>
<tr>
<td>Picric Acid</td>
<td>&gt; 60 cm</td>
<td>&gt; 24 cm</td>
</tr>
</tbody>
</table>

C₆H₅N₂O₆, mw 243.14, N 28.81%, OB to CO₂ 55.9%, ye needles or plates from alc, mp 280–288° (decomp 301°).

It was prep'd in 1884 by Nölting and Collin (Ref 2) from ethyl- or methyl-esters of Syphnic Acid and alc ammonia. Blanksma (Ref 3) prep'd it from 3-chlor-2,4,6-trinitroanisole (or 3-chlor-2,4,6-trinitrophenetole) and alc ammonia, Köhner and Contardi (Ref 4) from 2,4-dibrom- (or dichlor)-1,3,5-trinitrobenzene and alc ammonia, and Flärscheim (Ref 5) from tetrinitroaniline and ammonia.

C.F. van Duin et al (Ref 6) reviewed all of the methods previously used, and described the following method of prepn: "Mix 10g of finely pulverized trinitro-m-anisidine (or phenetidine) with 80ml of concd ammonia (d 0.909/cc) and leave for 24 hours at room temp. Shake frequently. Filter, wash the ppt with w to remove the ammonia, and boil with alc to remove traces of non-reacted TNA or TNPhen. The mp of the product should be around 285°, but it rises slightly to 287–288° if the product is recryst with gl acet ac" (See also Ref 1, pp 60, (17) & [33])

Except for being somewhat sol in acet ac and alc, it is nearly insol in all solvents.

Its expl properties were examined by van Duin et al (Ref 6) and are as follows:

**Explosion Temperature** (Ref 6, pp 169–171). Using the method prescribed by the Ger Railway Commission (see Vol 7, 126-L):

**Method A.** Temp 335° (by heating the bath at a rate of 20° per minute). TNT=321°, PA 316° & Tetryl 196°

**Method B.** Temp 320° (by heating the bath at a rate of 5° per minute). TNT=304°, PA 309° & Tetryl 187°

**Impact Sensitivity.** (Ref 6, pp 171–175). Using the Lenzke-Kast app (see Marshall 2 (1917), 423) at a temp of 19–23° with 33mg samples:

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Maximum Fall for 0/6 Shots</th>
<th>Minimum Fall for 6/6 Shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,6-Trinitro-m-phenylenediamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetryl</td>
<td>&gt; 60 cm</td>
<td>&gt; 24 cm</td>
</tr>
<tr>
<td>TNT</td>
<td>&gt; 60 cm</td>
<td>&gt; 24 cm</td>
</tr>
<tr>
<td>Picric Acid</td>
<td>&gt; 60 cm</td>
<td>&gt; 24 cm</td>
</tr>
</tbody>
</table>
Thermal Stability. When heated at 95° for 30 eight-hr days, no change in compn took place.


α-Phenylethanol (α-Phenylethyl alcohol, Methylphenyl carbinol). C₆H₅CHOH.CH₃, mw 122.16, liq, bp 203.6° at 475mm, d 1.019g/cc at 13/4°. Prepn and other properties are given in Beil 6, 475, (236) & [445]

β-Nitro-α[2-nitrophenyl]-ethanol nitrate (α-[2-Nitrophenyl]-β-nitroethanol nitrate, 1-[α-Nitrophenyl]-2-nitroethanol nitrate).

(O₃N)C₆H₄.CH(ONO₂).CH₂.NO₂, mw 257, N 16.4%, OB to CO₂ –77.8%, pale yel crystals, mp 132–133°. Sol in acet-alc and is decompd by warm w. Can be prepd by nitrating the condensation product of α-nitrobenzaldehyde and nitromethane in the presence of trimethylamine.

It is an expl with a ballistic strength about 99% that of TNT, and its sensitivity is comparable to that of Tetryl. Its thermal stability is unsatisfactory, and its hygroscopicity is slight. Refs: 1) Beil—not found 2) L.F. Fieser et al., OSRD 176 or PBL 31091 (1941), 9–12

β-Phenylethanol (Benzylcarbinol). C₆H₅.CH₂.CH₂.OH, mw 122.16, colord oil, bp 219–221° at 750mm, d 1.023g/cc at 13/4°, sol in alc and eth. Methods of prepn are given in Beil. Nitrination of this product resulted in an oily product which expld from a hammer blow. It was probably impure trinitrophenylethanol (see below).

Ref: Beil 6, 478, (237) & [448]

β-[2,4,6-Trinitrophenyl] ethanol (2,4,6-Trinitro- benzylcarbinol). (O₃N)C₆H₄.CH₂.CH₂.CH₂.OH, light yel crystals, mp 112°, sl sol in w, sol in benz & toluene. It was prepd by heating α-TNT with formaldehyde in weak alkaline soln. Its expl properties have not been examined. On nitration it gives the expl:

β-[2,4,6-Trinitrophenyl] ethanol Nitrate (β-[2,4,6-Trinitrophenyl] ethyl nitrate).

(O₃N)C₆H₄.CH₂.CH₂(ONO₂), mw 302, N 18.5%, OB to CO₂ –53.0%, crystals, mp 83°. It was prepd by Vender (Ref 2) by nitrating the above trinitrophenyl alcohol. It is an expl which can be detonated by heat or impact.

Refs: 1) Beil 6, (239) 2) V. Vender, Gazz 45, II, 97 (1915); ibid, JCS 106, I, 956 (1915) 3) Blatt, OSRD 1944

Phenylether or Phenylxide. See under Diphenylether and Derivatives in Vol 5, D1352-R ff

Phenylethylamine. See under Ethylaniline and Derivatives in Vol 6, E206-L ff

Phenyletheneglycol (Phenylglycol). C₆H₅.CH(OH).CH₂.OH, needles or lgg, mp 67–68°, bp 272–274° at 755mm. Sol in w, alc, benz, eth, chl & acct ac; sl sol in lgg. Can be prepd by heating styrene dibromide, C₆H₅.CHBr.CH₂.Br, at 125° with Pb acetate and acct ac, and then heating the resulting acetate with K carbonate soln (Refs 1 & 2). Other methods of prepn are given in Ref 3.


Phenyletheneglycol Nitrated Products. Nitration of phenyletheneglycol with mixed nitric-sulfuric acid gave an expl product, mp ca 85°, which was claimed to be 110% as powerful as TNT, as detd by the Trauzl test, and whose performance was intermediate between that of Tetryl and TNT (Ref 1).

Fishbein’s subsequent investigations (Ref 2) showed that this expl consisted of about 80% mononitrophenyglycol dinitrate,
(O₂N)C₆H₄.CH(ONO₂)CH₂(ONO₂), and about 20% dinitrophenylglycol dinitrate, (O₂N)₂C₆H₃.CH(ONO₂).CH₂(ONO₂)

This mixt, as well as other nitro-nitrates of aryl-substituted polyhydric alcohols, was recommended for use in exps, either alone or with appropriate additives, eg, in propillers, primer compns, detonators, etc.

It was suggested that trinitrophenylglycol dinitrate, (O₂N)₂C₆H₂.CH(ONO₂).CH(ONO₂), might be prep'd by further nitration.

Refs: 1) Westfälisch-Anhaltische Sprengstoff AG, GerP 558126 (1932); ChemZtr 1932, II, 3185 2) M.S. Fishbein, Voyennaya Khimia (Russia), No 6, 3–8 (1933); ChemZtr 1934, II, 1074–5 & CA 29, 7077 (1935)

Phenylethelyenglycolether Derivatives. See under β-Phenoxyethanol and Derivatives in this Vol

bis [(Phenylethelyenglycol)-ether Derivatives. See under Ethylene glycol Diphenylether in Vol 6, E 255-R

Phenylglycolether Derivatives. See under β-Phenoxyethanol and Derivatives in this Vol

Phenylguanidine. C₆H₅.NH.C(:NH).NH₂, mw 135.19, monoclinic crs, mp 65–67°. Prepn and other properties are given in Beil 12, 369, (235) & [216]

Dinitrophenylnitroguanidine. (O₂N)₂C₆H₅.NH.C(:NH).NH(NO₂), mw 258.19, N 27.90%, OB to CO₂ –68.2%, crs from alc, mp 175–178°. It was prep'd by Elderfield et al (Ref 2) by gradually adding 2g of nitrophenylguanidine sulfate (dissolved in 5ml concd sulfuric acid) to 10ml of fuming nitric acid (d 1.5g/cc) at such a rate that the temp remains at 10°.

The mixt was then stirred for 30 minutes at 25–30°, then for 45 minutes at 45–50°, and finally drowned in ice w. It is an expl

2,4,6-Trinitrophenylguanidine (Picrylguanidine). (O₂N)₂C₆H₅.NH.C(:NH).NH₂, mw 270, N 35.3%, OB to CO₂ –65.3%. Prepd by the action of cyanamide on trinitroaniline. Reported impact sensitivity, FI 110% of PA. It was too reactive for use as a HE (Ref 4)

N-2,4,6-Trinitrophenyl-N'-nitroguanidine.

(O₂N)₃C₆H₂.NH.C(NH).NH(NO₂), mw 315.19, N 31.11%, OB to CO₂ –43.1%, color crs, mp 225–226° (decomp). Can be prep'd by heating a soln of 5g of dinitrophenylnitroguanidine in mixed acid (5ml sulfuric, 20ml nitric, d 1.5g/cc) for 1 hr at 80°, and then pouring onto ice. Another method is the one step nitration of nitrophenylguanidine sulfate, as described in Ref 3

Trinitrophenylnitroguanidine expld with a bright flash and little smoke when heated in an open dish, or when struck by a hammer on an Fe plate.

Refs: 1) Beil 12—not found 2) R.C. Elderfield et al, OSRD 158 or PBL 31085 (1941), 18–21 3) Ibid, OSRD 907 or PBL 31094 (1942), 12–13 4) Blatt, OSRD 2014 (1944)

Phenylhydrazine and Derivatives. See under Hydrazinobenzene and Derivatives in Vol 7, H 207–L ff

2,4,6-Trinitrophenylmethoxytrinitramine (Tetroxyl).

C₇H₅N₅O₉, mw 303, N 23.1%, OB to CO₂ –49.6%. Sensitivity to impact, FI 36% of PA. Pb block expansion, 131% of PA.

Refs: 1) Beil—not found 2) Blatt, OSRD 2014 (1944)

Phenylmethyl Ether, Nitrated Compounds. See under Anisole and Derivatives in Vol 1, A 448–L ff

Phenyltrimine (Nitranilide, Diazobenzolic Acid).

C₆H₅.NH.NO₂, mw 138.13, N 20.28%, OB to CO₂ –150.6%, wh leaflets, mp 46–46.5°, expls on rapid heating. Sol in w, sl sol in cold lig, v sol in alc and other org solvents. Can be prep'd by the action of N₂O₅ on an ethereal soln of aniline at –20°, or by other methods. Its Ag
2-Nitrophenylnitramine. \( O_2N.C_6H_4.NH.NO_2 \), mw 183.12, N 22.95%, OB to \( CO_2 \) -91.2%, pale yel needles or brownish yel plates, mp 65.5\(^\circ\), explds on rapid heating. Can be obtained by nitrating 2-nitroaniline with nitric acid and Ac\(_2\)O. Forms salts, some of which are expl.

3-Nitrophenylnitramine. Pale yel needles, mp 92\(^\circ\), explds on rapid heating. Can be prepared by nitrating 3-nitroaniline as above. Forms salts, some of which are expl.

4-Nitrophenylnitramine. Pale yel needles, mp 110–111\(^\circ\), explds on rapid heating. Can be prepared by nitrating 4-nitroaniline as above. Forms salts, some of which are expl.

Ref{s}: 1) Beil 16, 666 2) E. Bamberger & E. Hoff, Ber 28, 401 (1895) 3) E. Bamberger, Ber 30, 1253 & 1256 (1897) 4) E. Hoff, Ann 311, 107–110 (1900)

2,4,6-Trinitrophenylnitramine (2,4,6-Trinitro-N-nitroaniline, Picrylinitramine). \( (O_2N)_3C_6H_2.NH.NO_2 \), mw 273.12, N 25.64%, OB to \( CO_2 \) -32.2%. Golden yel crystals, mp explds <90\(^\circ\), easily sol in eth and most other org solvents. Can be prepared by the action of K nitrite on 2- or 4-nitroaniline, dissolved in sulfuric acid monohydrate, cooled to 5\(^\circ\).

It is a very powerful and sensitive expl. Forms salts, some of which are expl.

Ref{s}: 1) Beil 16, 688 2) O. Witt & E. Witte, Ber 41, 3090–94 (1908)

2,4,6-Trinitrophenylbutylnitramine. See under “Butyl Tetryl” in Vol 2, B379-R

2,4,6-Trinitrophenylethylnitramine. See under “Ethyl Tetryl” in Vol 6, E207-L & E319-R

2,3,4,6-Tetranitrophenylnitramine. \( C_6H_2N_6O_{10} \), mw 318, N 26.4%, OB to \( CO_2 \) -15.1%, mp 98\(^\circ\), decomps. It was prepd prior to WWII in Engl and was considered too reactive and sensitive for consideration as a mil HE. Pb block expansion 170% PA

Ref{s}: 1) Beil—not found 2) Blatt, OSRD 2014 (1944)

Phenylnitromethane. \( C_6H_5.CH_2.NO_2 \), mw 137.13, N 10.21%, yel liq; bp 135\(^\circ\) at 25mm and 141–2\(^\circ\) at 35mm (with slight decomps); d 1.160g/cc at 20/0\(^\circ\). Can be prepared by heating toluene with dil nitric acid (d 1.12g/cc) in a sealed tube (Ref 2) or by other methods (Ref 3 & 4)


3,5-Dinitrophenylnitromethane, \( (O_2N)_2C_6H_3.CH_2(NO_2) \), mw 227.14, N 18.50%, OB to \( CO_2 \) -74.0%; nearly colorl, large flat plates; mp 130–132\(^\circ\). Was first prepd by Holleman (Ref 2). Later, Urbanski (Ref 3) prepd it by nitrating 3-mononitrophenylnitromethane with fuming nitric-sulfuric acid, which in turn was obtained by treating phenylnitromethane with fuming nitric acid at 15\(^\circ\). Fieser et al (Ref 4) verified Urbanski’s method, obtaining yields of 71–73.5%

Dinitrophenylnitromethane is an expl with about the same power as TNT, but is more sensitive to impact. It is very stable to heat. It ignites at about 343\(^\circ\) when heated unconfined at the rate of 10\(^\circ\) per minute. Some of its salts are expl.

Ref{s}: 1) Beil—not found 2) A.F. Holleman, Rec 14, 121 (1895) 3) T. Urbanski, CR 206, 1124 (1938) & CA 32, 4959 (1938) 4) L. Fieser et al, OSRD 176 (1941), 2, 15 & 19 5) Urbanski 1, 598 (1964)
OB to CO$_2$ -74.0%, yellowish to colorless prisms, mp 121–130° (various investigators), d 1.29 g/cc, insol in w, sol in methanol and acet.

It was first prep by Milone & Massa (Ref 2) by nitrating phenyl nitromethane with strong nitric acid (d 1.52g/cc). Fieser et al (Ref 3) prep it using two methods: a) nitration of phenyldinitromethane; and b) by direct synthesis using the "Ponzo" reaction in which an ethereal soln of m-nitrobenzaldoxime is added dropwise and under reflux to an ethereal soln of nitrogen peroxide;

$$2(O_2N)C_6H_4.CH:NOH + 5NO_2 \rightarrow 2(O_2N)C_6H_4.CH(NO_2)_2 + 3NO + H_2O$$

The yield in the latter method was low, about 27.5%.

Its expl properties are given below:

**Ballistic Strength.** 100% TNT (BuMines)

**Explosion Temperature.** Does not expl or ignite at 360° or below

**Heat of Combustion.** 818.1 kcal/mole

**Hygroscopicity.** Practically none

**Impact Sensitivity.** Comparable to TNT

**Power.** By Trauzl test, 103% TNT

**Rifle Bullet Test.** No detonations from impact of 30 cal bullet at 90 ft

**Thermal Stability.** Unsatisfactory, loses 49% of wt in 48 hrs at 75° (International Test)

**Velocity of Detonation.** No information

**Salts of (m-Nitrophenyl)nitromethane.** Milone and Massa (Ref 2) prep several metallic salts and found that their expl power decreased with increasing atomic wt of the metal. Following are some of the expl salts: K salt—yellow crystals; Ag salt—golden yellow crystals; Ba salt—yellow needles; Pb salt—orange yellow ppt; Apm salt—yellow flakes. In general, the salts are more sensitive and less powerful than the parent compd


1,3-Phenyloxazol-2 yl-benzenediazonium hydroxide(2). H$_3$C—N

$$C_6H_5.C.O.C_6H_5.N(\cdot)OH$$

(derivative of oxazole). Its chloride, C$_{15}$H$_{11}$ON$_3$Cl, orange colored crusts with mp 128° (decomp), can be prep by treating 5-phenyl-2-[2-aminophenyl] oxazole with isoamyl nitrate and eth. This diazonium chloride forms a stable aurichloride salt, C$_{15}$H$_{11}$ON$_3$+AuCl$_3$, which melts and then expls at about 163°

**Refs:** 1) Beil 26, (441) 2) J. Lister & R. Robinson, JCS 101, 1311 (1912)

2-Nitro-2-(3′-nitrophenyl)-propanediol-1,3-dinitrate (2-Nitro-2-(m-nitrophenyl)-propane-1,3-diol-dinitrate). (O$_2$N)$_2$C$_6$H$_4$.C(NO$_2$)$_2$:(CH$_3$.ONO$_2$)$_2$, mw 332, N 16.9%, OB to CO$_2$ -57.8%, pale yel acicular prisms, mp 71–73.6°. Can be prep by nitrating 2-nitro-2-(3′-nitrophenyl)-propanediol-1,3 with mixed nitric-sulfuric acid, as described in Ref 2, p 23. Sol in most common organic solvents

It is an expl, having a ballistic strength of 114% (TNT=100); impact sensitivity—less sensitive than TNT; friction sensitivity—no detonations; ignition temp—270°; practically non-hygroscopic and of satisfactory thermal stability


2-Nitro-(3′,5′-dinitrophenyl)-propanediol-1,3-dinitrate. (O$_2$N)$_2$.C$_6$H$_3$.C(NO$_2$)$_2$:(CH$_3$.ONO$_2$)$_2$, mw 377.19, N 18.57%, OB to CO$_2$ -40.3%; yellowish, flat, rectangular plates (sometimes prisms); mp 114–115.8°, d 1.70g/cc. Sol in acet, sl sol in cold alc. Qc 1022.9 kcal/mole

Can be prep by gradually adding, over a 6 minute period, 20g of 2-nitro-2(3′,5′-dinitrophenyl)-propanediol-1,3 to 130ml of fuming nitric acid (d 1.5g/cc), cooled to 5° (this raises the temp to about 10°). This mixt is drowned in 1.5g of ice w, and after about 15 minutes, the gummy solid is washed with cold w. The gummy material is dissolved in acet, and the soln filtered and dill with alc until the first appearance of turbidity. Crystn occurs when the suspension is allowed to stand

It is an expl comparable to Tetryl in strength, and to PETN in sensitivity to mechanical action

**BalMort Test.** 126% TNT

**Explosion Temp.** Ignites but does not expl at about 360°
Friction Sensitivity. Comparable to Cyclonite

Hygroscopicity. Practically non-hygroscopic

Impact Sensitivity. Slightly less sensitive than PETN

Thermal Stability. Satisfactory


**4-Nitrophenylpropionic Acid.**

(O$_2$N)C$_6$H$_4$.C:C:COOH, mw 191.14, N 7.33%, needles from alc or eth, mp 181$^\circ$ (decomps explosively on further heating). Easily sol in hot alc, acet ac or eth, very sl sol in carbon disulfide, difficulty sol in w, benz and chl, insol in pet ether

Can be prep by treating phenylpropionic acid, C$_6$H$_5$.C:C:COOH (Beil 9, 633, (265) & [436]) with nitric acid (d 1.5g/cc) at $-20^\circ$ (Ref 3) or by other methods (Refs 1 & 2)

It is a weak exp and forms salts which are more or less expl:

**Ba salt.** Needles, insol in w; puffs off on heating

**Ca salt.** Needles, puffs off on heating

**Ag salt.** Yel amorph powder; puffs off violently on heating; ignites on contact with concd sulfuric acid


**2,4,6-Trinitrophenyl (β,γ-Dinitroxy) Propyl-nitramine.** C$_6$H$_5$.N$_2$.O$_4$. mw 437, N 22.4%, O$_2$NNCH$_2$.CH(ONO$_2$.CH$_2$.ONO$_2$.O

OB to CO$_2$ $-27.4%$. Can be prep by condensing aniline with glycerol, and the product nitrated. Ref 2 states that this material has adequate stability and sensitivity, together with "the greatest power of any known nitro compound"

Refs: 1) Beil—not found 2) Westfälisch-Anhaltische Sprengstoff AG, GerP 576152 (1933) & CA 27, 3823 (1933) 3) Blatt, OSRD 2014 (1944)

**2,4,6-Trinitrophenyl-(1-Methylol) Propyl-nitramine Nitrates.** C$_{10}$H$_{16}$.N$_2$.O$_3$.N$_2$.Cl, mw 390,

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{N(NO}_2)\text{CHCH}_2\text{CH}_3 \\
\text{N}_2\text{Cl} & \quad \text{CH}_2\text{ONO}_2
\end{align*}
\]

N 21.5%, OB to CO$_2$ $-57.4%$, mp 140$^\circ$ (decomp). Can be prep by condensing dinitrochlorobenzene and 2-amino-1-butanol, and nitrating the product

Its impact sensitivity is comparable to Tetryl; BalMort 117% TNT. It ignites at 210$^\circ$, but does not expl to 360$^\circ$. It expls in 30 minutes at 135$^\circ$, but no expln results after 300 minutes at 100$^\circ$. At 25$^\circ$, it gains 0.19% by wt at 100$^\circ$ relative humidity

Refs: 1) Beil—not found 2) Blatt, OSRD 2014 (1944)

**[1-Phenyl,3-ethyl-tetrazene](1) [(3-Ethyl, 1-phenyl)-tetrazene](1), Benzdiazao-[α-athyldiazoo]id or 3-Aethyl-1-phenyltetrazene(1) in Ger].

C$_6$H$_5$.N:NN(C$_2$H$_5$).NH$_2$. mw 164.24, N 34.12%, oily liq, bp expls. Was prep by Fischer and Troschke in 1879 (Ref 2) by introducing a benzene-diazonium salt into a cold ag soln of ethlyhydrazone. It is sol in eth and is depnked by alkalis. A very unstable compd, which deflagrates on rapid heating. It forms salts which are also unstable

Refs: 1) Beil 16, 746 2) E. Fischer & H. Troschke, Ann 199, 306--7 (1879) 3) E. Fischer, Ber 43, 3500 (1910)

Phenylaminotetrazoles. See under Aminophenyltetrazoles and Derivatives in Vol 1, A246-R to A249-L

**1-Phenyl-tetrazole.** mw 146.17, N 38.34%, crsryls HC.N(C$_6$H$_5$).N from ag alc or benz

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*}
\]

\[N———N\]

from wth lgr, mp 65--66$^\circ$.

Can be prep by the oxidation of 1-phenyl-5-mercaptopetrazole with Cr trioxide in boiling acl, or by treating sym diformylhydrazide, OHC.NH.HN.CHO, and benzenediazonium chloride, C$_6$H$_5$.N$_2$.Cl, with dil Na hydroxide soln. Insol in w, diff sol in lgr, sol in methanol, ethanol, chl, acet and benz
[1-(p-Nitrophenyl)]-tetrazole (Called 1-[4-Nitrophenyl]-tetrazole by Beil). Mw 191.17, N 36.64%, HC.N(C₆H₄NO₂).N OB to CO₂ 121.4%, N—N —N (with violent decomp). Can be prepd by the nitration of 1-phenyltetrazole with fuming nitric acid, or by heating sym-diformyl-hydrazine, OHC.HN.NH.CHO, and p-nitrobenzenediazonium chloride, O₂N.C₆H₄.N₂Cl, with dil Na hydroxide soln. Insol in w and lgr, diff sol in benz and eth, sol in ethanol and methanol, v sol in acct. Puffs off when heated above its mp


2-Phenyl-tetrazole. Mw 146.17, N 38.34%, liq, bp HC:N(C₆H₄) (puffs off on heating above 170°). Can be prepd by heating 2-phenyl-5-carboxy-tetrazole (Beil 26, 560) to 150–170°. Nearly insol in w; sol in conc acids, alc & eth

Refs: 1) Beil 26, 347 2) J.A. Bladin, Ber 18, 2911 (1885) 3) E. Wedekind, Ber 31, 948 (1898) 4) F.R. Benson, Chem Revs 41, 5 (1947)

5-Phenyl-tetrazole. Mw 146.17, N 38.34%; white (C₆H₄).C.NH.N—N —N —N—N (thomb-pyramidal crysts; mp 213–15° (decomp)). Can be prepd by treating benzohydrazide-imide, C₆H₅.C(NH).NH.H₂ (Beil 9, 328), with Na nitrite plus HCl or HNO₃, or by treating N,N'-bis [α-amino-benzyl] hydrazine, C₆H₅.C(NH).NH.H₂ (Beil 9, 329), with Na nitrite plus acetic acid. Nearly insol in cold w, benz and petr eth; sl sol in hot w and in eth; sol in alc. Decomp explosively on rapid heating above about 250°

Forms salts, some of which are expl:

Calcium salt. Ca(C₆H₅N₄).H₂O. Needles from alc and eth. Loses w at 140–150° and then expls without melting (Ref 1)

Copper salt. Cu(C₆H₅N₄). Crysts, mp decomp at 130° and deflagrates when heated rapidly on a Pt foil

Other salts are also known, such as the NH₄, Ba, K and Ag, but they have not been reported as being expl

5-Phenyl-tetrazole also forms nitrocompds, such as:

[5-(m-Nitrophenyl)]-tetrazole (Called 5-[3-Nitrophenyl]-tetrazole by Beil). Mw 191.17, N 36.64%, (O₂N.H.C₆H₄).C.NH.N OB to CO₂ 121.4%, mp 145° (when heated under N —N w). Was prepd by Lossen & Statius (Ref 4, p 104) by treating 5-phenyl-tetrazole with nitric acid (d 1.5g/cc). V sol in alc, sol in eth and hot w, insol in benz. Expls on heating above its mp. It forms salts, some of which are expl:

Silver salt. AgC₆H₄(NO₂). Pale yel solid which puffs off on heating on a Pt foil (Ref 1, p 364)


[1-Phenyl; 5-azido]-tetrazole. Mw 187.19, N N(N(C₆H₄)).C.N₃ 52.39%, leaflets, mp 99°. Can be prepd by adding N —N —N —N —N dropwise, a soln of Na nitrite to a well-cooled HCl soln of phenyl-1-hydrazine-5-tetrazole. Insol in w, sl sol in eth, sol in hot alc, sl sol in cold alc. Puffs off with a loud report when heated rapidly in a sealed tube

Ref: 1) Beil—not found 2) R. Stolle, JPrakt-Chem 134, 284 & 297 (1932)

[2-Phenyl, 5-carboxy]-tetrazole. Mw 182.18, N (HOOC).C:N(N(C₆H₄)). 30.76%, mp, for the anhydr salt, 137–38° (decomps at about 150°). Crystallizes from w as needles with one H₂O, but loses it on desiccator drying. Was prepd by Bladin in 1885 (Ref 2) by heating 2-phenyl, 5-cyanotetrazole with alc KOH. Wedekind prepd it by the oxidation of 2-phenyl-5-[4-aminophenyl]-tetrazole with K permanganate in warm dil nitric acid (Ref 3)

Sol in w, v sol in methanol and alc, diff sol in eth

It forms salts, some of which are expl:

Copper salt. Cu(C₆H₄O₂N₄).2H₂O. Greenish-
blue plates, losing w at 125° and exploding at higher temps
Silver salt. AgC₆H₅O₂N₄. Colorl. powder, puffs off on heating
Phenylcarboxytetrazole forms nitrocompds,
such as:

\[
\begin{align*}
\text{[2-(p-Nitrophenyl), 5-carboxy]-tetrazole} & \quad \text{(Called} \\
\text{2-[4-Nitrophenyl]-carbonsûure-(5) by Beil)} \\
\text{(HOOC).C.N(C₆H₄NO₂).N} & \quad \text{N—N} \\
\text{N—} & \\
\text{Mw 235.18, N 29.78%, mp 175° (decompn).} & \\
\text{Can be prep'd by treating 2-phenyl, 5-carboxytetrazole with fuming nitric acid} & \\
\text{Rathsburg (Ref 5) patented some expl salts} & \\
\text{and derivatives of phenylcarboxytetrazole, which he called phenyltetrazole-carboxyllic acid, for use} & \\
\text{in detonators and percussion caps} & \\
\text{Refs: 1) Beil 26, 560} & \\
\text{2) J.A. Bladin, Ber 18,} & \\
\text{2908 (1885); 25, 1411 (1892)} & \\
\text{3) H. Wedekind, Ber 31, 943 (1898)} & \\
\text{4) O. Dimroth et al, Ber 41, 4057-58, 4066-68 (1909)} & \\
\text{5) H. Rathsburg, BritP 185555 (1922) & CA 17,} & \\
\text{1147 (1923)} & \\
\text{[1-Phenyl(3-α-"ethylpropionate"), 4-carboxyamido]-tetrazene(1). Note: α-ethylpropionate} & \\
\text{(or more correctly, in the opinion of the editor, α-ethylpropionatyl) is the proper name for the} & \\
\text{radical -CH(CH₃)CO₂C₂H₅, derived from α-propionic acid ethyl ester.} & \\
\text{(C₆H₅).N-N[CH(CH₃)CO₂C₂H₅].NH(CO.NH₂),} & \\
\text{mw 279.34, N 25.08%, crysts from aq alc, mp} & \\
\text{melts with expn ca 125°) & \\
\text{Was prep'd by Bailey and Knox (Ref 2) from} & \\
\text{benzenediazonium chloride and α-secarbazinopropionic acid ethylester (Beil 4, 557)} & \\
\text{Sol in alc, ethyl acetate & chlf; sl sol in eth;} & \\
\text{insol in benz & petr eth} & \\
\text{Refs: 1) Beil 16, 747} & \\
\text{2) J.R. Bailey & L.} & \\
\text{Knox, JACS 29, 884 (1907)} & \\
\text{[2-Phenyl, 5-methyl]-tetrazole (Was called 1-} & \\
\text{Phenyl-4-methyl-tetrazol by Dimroth, Ref 2).} & \\
\text{(CH₃)C:N.N(C₆H₅) Mw 160.20, N 34.98%,} & \\
\text{| |} & \\
\text{N—N} & \\
\text{N—} & \\
\text{At 15mm. Can be prep'd by treating 2,4,6-tri-} & \\
\text{brom-1-azidobenzene with acetaldehyde phenyl-} & \\
\text{hydrazone in Na ethylate soln. Sol in eth and} & \\
\text{fuming nitric acid. Decomp's explosively on} & \\
\text{distn at atm press} & \\
\text{Refs: 1) Beil 26, (111) 2) R.G. Faragher &} & \\
\text{R. Furness, JCS 107, 689 & 695 (1915)} & \\
\text{3) F.R. Benson, ChemRev 41, 5 (1947)} & \\
\text{5-Picrylamidotetrazole. Mw 296.19, N 37.84%,} & \\
\text{C₆H₂(NO₂)₃.NH.C.NH.N} & \\
\text{N—N} & \\
\text{Pale yel crysts, mp 224°. Can be prep'd by heating} & \\
\text{5-aminotetrazole with picryl chloride in acetic acid} & \\
\text{soln under reflux for 2 hours. Sl sol in w} & \\
\text{and alc, easily sol in acetic, nearly insol in eth} & \\
\text{It forms salts, some of which are expl:} & \\
\text{Silver salt. On treating a soln of picrylamidotetrazole in acetic acid with a small excess of aq} & \\
\text{Ag nitrate soln, a yel ppt is obtained which} & \\
\text{corresponds to the formula C₇H₅O₆N₆ Ag,} & \\
\text{N=27.89%. It is insol in nitric acid and difficul-} & \\
\text{tly sol in ammonia. It detonates violently} & \\
\text{on heating in a sealed tube or on impact} & \\
\text{Its Cu and Pb salts were also prep'd, but not} & \\
\text{analyzed. Both of them expld on heating in a} & \\
\text{sealed tube or on impact, and seem to be suitable} & \\
\text{for use as initiating agents (Ref 2)} & \\
\text{Refs: 1) Beil—not found} & \\
\text{2) R. Stolilé & O.} & \\
\text{Rosser, JPraktChem 139, 63—4 (1933)} & \\
\text{3) F.R.} & \\
\text{Benson, ChemRev 41, 7 (1947)} & \\
\text{Pyrido-1',2',4',5-tetrazole. (Called 1,2,3,9-Benzo-} & \\
\text{isotetrazole by Faragher & Furness (Ref 2),} & \\
\text{and Pyridotetrazole by Benson (Ref 3); 1,2,3-} & \\
\text{Triaza-indolizin or Benzotetrazol in Ger).} & \\
\text{HC:CH.C:N:N Mw 120.13, N 46.65%,} & \\
\text{| | | | | | |} & \\
\text{Prisms, mp 159°. Was} & \\
\text{HC:CH.N—N prep'd by Faragher and} & \\
\text{Furness (Ref 2) by treating a cooled acetic acid} & \\
\text{soln of 2-pyridyldihydrazine with an aq soln of} & \\
\text{Na nitrite. Nearly insol in cold w and eth, sol} & \\
\text{in alc and acet. Explds when touched with a} & \\
\text{hot wire} & \\
\text{Refs: 1) Beil 26, (111) 2) R.G. Faragher &} & \\
\text{R. Furness, JCS 107, 689 & 695 (1915)} & \\
\text{3) F.R. Benson, ChemRev 41, 5 (1947)} & \\
\text{Phenyltriazene. C₆H₅.N:N.NH₂, mW 121.16,} & \\
\text{N 34.69%, colorl crysts, mp 50° with rapid}
decompn. Can be prep'd by reduction of azido-benzene, using Sn chloride, as described in Ref 2. It is very unstable, even at room temp. Forms salts, some of which are expl:

- **Copper salt**: \( \text{C}_6\text{H}_5\cdot\text{N}_3\text{Cu} \); yel crystals; deflagrates on heating without melting
- **Silver salt**: \( \text{C}_6\text{H}_5\cdot\text{N}_3\text{HAg} \); deflagrates on standing at room temp

Refs: 1) Beil 16, 685–6 2) O. Dimroth, Ber 40, 2378–9 (1907)

1-Phenyl-1-oxy-III-benzenesulfonfyl-triazine
(3-Benzolsulfonfyl-1-phenyltriazan-1-oxoy-1 in Ger). \( \text{C}_6\text{H}_5\cdot\text{O}^\cdot\text{N}^\cdot\text{N}\cdot\text{NH}^\cdot\text{SO}_2^\cdot\text{C}_6\text{H}_5 \), mw 277.32, N 15.15%, needles, mp decamps 102°. Can be prep'd from \( \text{N}_3\text{N}^\cdot\text{N}^\cdot\text{dibenzolsulfonylhydratene} \) and nitrobenzene in the presence of alkali. It explosd very violently on rapid heating or on impact

Refs: 1) Beil 16, (414) 2) A. Angeli, Atti AccadLinceiRend (5), 24, 1, 1098 (1915); JCS 108 (Abs 1), 847 (1915)

1-Phenyl-III-p-phenylmercaptotoly-triazine (N'-Phenyl-N-p-phenylmerceptotoly-triazine). \( \text{C}_6\text{H}_5\cdot\text{N}^\cdot\text{N}^\cdot\text{NH}^\cdot\text{C}_6\text{H}_5\cdot\text{S}^\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 \), mw 319.45, N 13.16%; yel crystals from aq alc; mp 85°; bp, puffs off on rapid heating. Sol in alc and ethh. Was prep'd from the benzenediazonium hydrochloride, Na acetate, and [4-aminophenyl-p-tolyllsulfide (Beil 13, 534). It explosd on rapid heating above its mp


Phenylbenzotriazoles. See under Benzophenyltriazole and Derivatives in Vol 2, B78-R to B79-R

1-Phenyl-4-nitro-5-nitraminobenzotriazole. See under Aminobenzotriazoles and Derivatives in Vol 1, A190-R

Phenyltoluidines. See under Anilinotoluene; Diphenylmethylamines and Derivatives in Vol 1, A438-L ff

Phenylurea and Its Nitrocompounds. See under Urea

Phermex. A 20-MeV, high intensity, high current flash radiographic app which was designed and built to complement other hydrodynamic facilities of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico. See Vol 4, D342-R for further information and a schematic diagram


Phlegmatization of Explosives. See under Desensitization (Phlegmatization) of Explosives in Vol 3, D88-L to D90-L, and Microencapsulation in this Vol

Phloroglucinol (1,3,5-Trihydroxy benzene, 1,3,5-Trioxo-benzol in Ger). \( \text{C}_6\text{H}_3\cdot\text{(OH)}_3 \), mw 126.11, white to yellowish crystals; mp 200–209° when heated slowly; 212–217° when heated rapidly; bp, sublimes with decompn. Sol in w, sol in alc and eth. Combustible. Can be prep'd by fusion of resorcinol with caustic soda, or by reduct of trinitrobenzene. It is highly toxic by ingestion, inhalation and skin absorption, and is a strong irritant to skin and mucous membranes


Trinitrochloroglucinol (sym-Trinitrotrohydroxy benzene. \( (\text{O}_2\text{N})_3\text{C}_6\text{OH} \), mw 261.11, N 16.09%, OB to CO\(_2\) 27.6%; yel needles with 1 mole H\(_2\)O from w; mp 167° (hydrate), 187° (with decomp for anhydr salt). Easily sol in hot w, alc, eth or benz. Expls when heated above its mp

Sorm and Drapalova (Ref 8) prep'd it by boiling 1,3,5-trichloro-2,4,6-trinitrobenzene (or triminotrinitrobenzene) with an alc NaOH soln.
Can also be prepd by treating phloroglucinol triacetate with nitric acid, or by other methods (see Ref 1).

It forms metallic salts which are more or less expd, such as Ba, Cd, K, Na and Pb, the last of which is described separately below.


**Trinitrophloroglucinol, Lead Salt of**

(Lead Trinitrophloroglucinate, Blei-trinitrophloroglucinat in Ger, Trinitroglucinate de plomb in Fr). \( [\text{C}_6\left(\text{NO}_2\right)_3\text{O}_3]_2\cdot\text{Pb}_3\cdot\text{H}_2\text{O} \), after drying at 145-150°C; Pb 53.77%; d 4.15g/cc at 30°C; mp explnds at about 210°C (Ref 7).

Ficheroule and Kovache (Ref 8) prepd the Pb salt by dissolving 2g of trinitrophenolglycolin in 50ml of w and adding, under mechanical agitation, 0.85g of NaOH. After bringing the soln to a boil, a soln of 3.80g of Pb nitrate in 50ml of w was gradually added while agitating. The soln was then cooled with agitation and the ppt sep'd by vacuum filtration, washed with w and dried, first in air at room temp, and then at 145-150°C.

**Solubility** (in percent at about 18°C). Water 0.12, methanol 0.05, pyr 0.06 & amyl acetate 0.04. Practically insol in benz, petr eth, chl, trichloroethylene, carbon tetrachloride, carbon disulfide, eth and acet.

Lead trinitrophloroglucinol is an expl, comparable in sensitivity to MF. According to Rathsburg (Ref 6), the impact sensitivity for the product contgt 54.5% Pb using a 100g wt was 10cm (1 detonation in 6 trials) vs 12cm for MF. For a product with 53.77% Pb, Ficheroule and Kovache (Ref 8) reported 30% detonations for a 2kg wt falling from a height of 70cm.

**Friction Sensitivity.** Required a load of 15kg/cm² for a steel surface, and 20kg/cm² for a procelain surface (corresponding figures for MF were 12-13kg and 15kg, respectively).

**Effect of heat.** When anhydrous, it detonates at about 210°C. The material with one H₂ O deフラ格ates about 230°C, when heated slowly, as compared to 275-290°C for Pb Staphenate. Contact with flame or a red-hot wire results in immediate detonation if the material is dry, but when wet it is difficult to detonate or ignite.

**Thermal stability and volatility.** No loss in wt was observed when stored for 300 days at 50°C, for 150 days at 70°C, or 50 days at 90°C.

**Hygroscopicity.** More hygroscopic than Pb Staphenate. When stored at 90% RH for 10 days it absorbed 0.24% moisture, and for 20 days, 0.90% moisture.

**Compatibility with metals.** Moderately moist material does not attack metals; it resembles Pb Staphenate in this respect.

**Compatibility with explosives.** Mixts with equal parts of TNT, PA, RDX, PETN, Tetryl, AN and Sb sulfide, stored for 40 days in a dry atm at 50°C, remained unchanged.

**Uses.** Pb trinitrophloroglucinol has been proposed as an ingredient of priming compns, and for use in percussion caps and detonator formulations (Refs 2, 3, 4, 5, 7 & 9).

**References:**

1) Beil 6, [1080] 2) H. Rathsburg, BritP 190215 (1921) & CA 17, 3101 (1923) 3) Ibid, USP 1470104 (1923) & CA 17, 3920 (1923) 4) W. Friederich, BritP 192830 (1921) & CA 17, 3255 (1923) 5) E. von Herz, GerP 377269 (1923)


**Phoenix Powders.** Safety expls patented in 1899 by Sprengstoff Dr. Nahsen & Co, Hamburg, Ger. One of the newer formulations contng NG 30, Na nitrate 32, and flour 38%. Its expl temp was 2125°C and its Qₜ was 780cal/g (Ref 1).
Naoûm (Ref 2) states that Phoenix Powders were a variety of Brit “Carbonités” (see Vol 2, C61-R) conqg NG 28–31, K nitrate or chlorate 30–34, NC 1, and woodmeal 33–37% 
Refs:  1) Daniel (1902), 449–50 [under Nañsen]  
2) Naoûm, NG (1928), 402 & 440

Phorone (Diisopropylidene acetone, 2,6-dimethyl-2,5-heptadien-4-one).  
\(\text{(H}_3\text{C})_2\text:C:CH.CO.CH:C(CH}_3\text{)}_2\), mw 132.80; yel liq or yellowish green prisms; mp 28°C, bp 198–199°C, flash pt 185°F, d 0.885g/cc at 20/4°C, vap pres 0.38mm at 20°C, RI 1.4968. V sol in w, sol in eth or alc. Combustible. Can be prep by methods given in Refs 1 & 2. It has been used as a solvent for NC.

When treated with ozone, it yields a very expl diozonide which ignites at room temp (Ref 2)  
Refs:  1) Beil 1, 751, (389) & [810]  
2) C. Harries & H.O. Turk, Ann 374, 338 (1910)  
3) Merck (1968), 823-L  
4) CondChemDict (1971), 686-L  
5) Sax (1975), 1020-R

Phosgene (CG, Carbonyl or chloroformyl chloride, Carbon oxyclyde). COCl\(_2\), mw 98.92; colorless, highly toxic gas; suffocating odor; when much diluted with air there is an odor reminiscent of moldy hay; fr pt –127.76°C, bp 8.2°C, d 1.392g/cc at 19/4°C. Sl sol in w and slowly hydrolyzed by it; freely sol in benz, toluene, gl acet acid, and most liq hydrocarbons. Can be prep by passing a mixt of carbon monoxide and chlorine over activated carbon, or by other methods described in Refs 1 & 8.

Phosgene was used tactically as a delayed or immediate action casualty gas. It was first employed by the Germans in WWI (Dec, 1915) in cylinders under the name D-Stoff. The French later (1916) employed phosgene as an artillery shell filler (Colligite). During the remainder of the war it was the Allies’ principal war gas, used also in trench mortars, bombs, and projector drums (Ref 2).

Vapor pressure. 1173mm Hg at 20°C; 555mm at 0°C; 365mm at –10°C.

Volatility. 442,000mg/m\(^3\) at –40°C; 2,200,000mg/m\(^3\) at –10°C; 6,370,000mg/m\(^3\) at 20°C.

Flashpoint. None

Decomposition temperature. 800°C

Latent heat of vaporization. 60cal/g

Rate of hydrolysis. Not readily hydrolyzed under usual field conditons; however, rain destroys its effectiveness. Heavy vegetation, jungle, and forests cause considerable loss of CG by hydrolysis on leaf surfaces.

Median lethal dosage. 3200mg-min/m\(^3\)

Median incapacitating dosage. 1600mg-min/m\(^3\)

Toxicology. In the presence of moisture, phosgene decomps to form HCl and CO. This action takes place within the body, when the gas reaches the bronchioles and the alveoli of the lungs. There is little irritant effect upon the respiratory tract, and the warning properties of the gas are therefore very slight. The liberation of HCl in the lungs tissues results in the development of pulmonary edema, which may be followed by bronchopneumonia, and occasionally lung abscess. Degenerative changes in the nerves have been reported as later sequelae. Concns of 3 to 5ppm of phosgene in air cause irritation of the eyes and throat, with coughing; 25ppm is dangerous for exposure lasting 30 to 60 minutes, and 50ppm is rapidly fatal after even short exposure.

There may be no immediate warning that dangerous concns of the gas are being breathed. After a latent period of 2 to 24 hours, the subject complains of burning in the throat and chest, shortness of breath and increasing dyspnea. Where the exposure has been severe, the development of pulmonary edema may be so rapid that the subject dies within 36 hours after exposure. In cases where the exposure has been less, pneumonia may develop several days after the occurrence of the accident. In subjects who recover, no permanent residual disability is thought to occur (Ref 12).

Disaster hazard. Phosgene is highly dangerous. When heated to decomp, or on contact with w or steam, it will react to produce toxic and corrosive fumes (Ref 12). Powdered Al burns in its vapor (Ref 3).

In the formation of tert-butyl azidoformate by the addition of phosgene to alcohols followed by the addition of Na nitride or hydrazoic acid in the presence of pyridine, reaction of phosgene with the azide can cause the formation of expl carbazide (Ref 9). Phosgene and 2,4-hexadiyn-1,6-diol react to form 2,4-hexadiyn-1,6-bischloroformate, which
is shock sensitive (Ref 11)

The reaction between isopropyl alcohol and phosphene forms isopropyl chloroformate and HCl. In the presence of Fe salts thermal decompm can occur, which in some cases can become expt (Ref 7)

Mellor (Ref 5) reports that a mixt of K and phosphene explds when subjected to shock, and that vapors of Na and phosphene react with luminescence at about 260°C (Ref 4)

The requirements of the US Armed Forces for phosphene are covered in specification MIL-P-10455A (18 Apr 1951), which covers two grades; Grade A – for use in munitions, max free chlorine 1.0%, and Grade B – for use in chemical manuf, max free chlorine 0.05%. Both grades are required to have a purity of 98.0% min, acidity (calcd as HCl) of 0.50% max, and residue on evaporation of 0.50%

Refs: 1) Beil 3, 31 2) Bebie (1943), 121

Phosphine (Hydrogen phosphide, Phosphorus trihydride). PH₃, mw 34.00; colorless gas, disagreeable, garlic-like odor; mp –133.5°C, bp –85°C, autoignition temp 100°F; d 1.185g/cc. Sparingly sol in cold w, insol in hot w, sol in alc and eth. Can be prepd by boiling yel P with an aq alkali hydroxide, or by the action of acids or w on metallic phosphides (Refs 8, 9 & 11)

Pure phosphine does not spontaneously ignite in air below 150°C unless it is thoroughly dried, when it ignites in cold air. The presence of traces (0.2%) of diphosphane (P₂H₄) in phosphine as normally prep'd causes it to ignite spontaneously in air, even at below –15°C (Ref 5). Pure phosphine is rendered flammable by a trace of di-nitrogen trioxide, nitrous acid, or similar oxidant (Ref 2)

Phosphine, generated by the action of w on Ca phosphide, was dried by passage thru towers packed with the latter. Soon after refilling the generator (but not the towers) and starting purging with argon, a violent expln occurred. This was attributed to the air, displaced from the generator by argon, reacting explosively with dry phosphine present in the drying towers, possibly catalyzed by the orange-yellow polypephosphate which forms on the surface of Ca phosphide (Ref 6)

Ignition occurs on contact with chlorine or bromine or their aq solns (Ref 3). The passage of phosphine into concd Ag nitrate soln causes ignition or expln, depending on the gas rate. Hg(NO₃) nitrate soln gives a complex phosphide, expl when dry (Ref 4). Phosphine is violently decompd by concd nitric acid, and flame is produced. Warm fuming nitric acid, dropped into a container of phosphine gas, produces an expln (Ref 1). Even small amts of oxygen present in phosphine results in an expl mixt, in which autoignition occurs at low pressure (Ref 7)

Phosphine is highly toxic by inhalation and is a strong irritant. Tolerance 0.3ppm in air (Refs 10 & 11)


Phosphorescence. See under Fluorescence, Luminescence and Phosphorescence in Vol 6, F124-R

Phosphorus (Red). PA(solid), mw 123.92; violet red, amorph or cryst powder; mp 597°C, subl at 416°C d 2.34g/cc; autoignition temp
about 260°, burns with formation of the pentoxide. Can be obtained from white P by heating at 240° with a catalyst. Insol in w, caustic alkali, CS₂, eth and ammonia soln (Refs 5 & 6)

Red P has been employed as an ingredient of pyrotechnic smoke, delay and safety match formulations (Refs 1, 2, 3 & 4). White smoke consisting of small droplets of phosphoric acid have been widely used for military purposes. These droplets result from the reaction of P pentoxide, formed by the burning in air of the P vapor (produced by the evaporation of Red P in a fuel-oxidant mixt) and w vapor in the air:

\[ P_4 + 5O_2 \rightarrow 2P_2O_5 \]
\[ P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \]
\[ H_3PO_4 + nH_2O \rightarrow H_3PO_4 \text{ (dilute)} \]
P vapor is extremely toxic and causes bone decay; however, it is not present after the smoke is formed. P pentoxide and phosphoric acid are not toxic in small concns, although they may be irritating to the eyes, respiratory tract and skin (Ref 3)

Red P is used in burning-type munitions mainly for signaling purposes. Compns consisting of red P and certain oxidants or fuels are relatively slow-burning and are sometimes used in sea markers. The chemical reactions may be quite involved. For example, the main reaction for a burning mixt of Ca sulfate and red P appears to be:

\[ 30CaSO_4\cdot19P_4 \rightarrow 6Ca(PO_3)_2 + 12Ca_2P_2O_7 + 10P_4S_3 \]
The heat produced by this reaction vaporizes the remaining Red P contained in the smoke mixt. The P vapor burns on contact with air. Some sulfur dioxide is formed when the \( P_4S_3 \), produced in the above reaction, burns along with the P vapor:

\[ P_4S_3 + 6O_2 \rightarrow 3SO_2 + 2P_2O_5 \] (Ref 3)

In the presence of moisture and air, there is a tendency for red P to slowly oxidize due to the presence of small quantities of Cu and Fe. This may result in ignition difficulty and an overall decreased performance of the smoke item. Stabilized red P has been produced which is not only low in Fe and Cu, but particles of less than 10 microns are mostly removed, and 2.5% of alumina is added as a stabilizer (Refs 3 & 4)

Red P is poisonous on inhalation or ingestion, but slower acting than white P. The lowest published lethal dose in man by oral ingestion is 1.4mg/kg (Ref 7). It should never be allowed to come in contact with the eyes. Red P, while less reactive than white P, is a dangerous fire hazard. It is easily ignited by spark or friction and is dangerous when in contact with organic materials or oxidizers. It can ignite spontaneously in air, and emits highly toxic fumes when heated (Ref 2)

The requirements of the US Armed Forces for red P are covered in two specifications, MIL-P-211B (18 June 1969) for Phosphorus, Red, Technical, and MIL-P-670A (18 Feb 1966) for Phosphorus, Red, Stabilized

**Table 1**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Percent by weight</th>
<th>Class 1</th>
<th>Class 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red phosphorus</td>
<td>99.0</td>
<td>99.0</td>
<td>99.0</td>
</tr>
<tr>
<td>White phosphorus</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Acidity(as H₃PO₄)</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Particle size:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retained on a No 40 (420 micron) sieve</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retained on a No 100 (149 micron) sieve</td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

MIL-P-670A covers one grade of aluminated red P furnished in powdered form, with the following requirements:

**Granulation.** Before aluminization – based on a selective sedimentation test, the phosphorus shall contain a max of 3% of particles of less than 10 microns in diameter. After alumination the powder shall pass thru the following sieves:

<table>
<thead>
<tr>
<th>Thru US Standard Sieve No</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>98.0 min</td>
</tr>
<tr>
<td>140</td>
<td>85.0 min</td>
</tr>
<tr>
<td>325</td>
<td>50.0 + 20</td>
</tr>
</tbody>
</table>

**Oxidation.** Based on the Norma-Hoff max oxidation bomb test, the phosphorus shall show the following oxidation characteristics: Induction period – the minimum induction period shall be 20 hours. Oxidation rate – the maximum
decrease in pressure per hour for a 5 gram sample shall be 1.4 psi for the visual method Copper and iron. The maximum content of either copper or iron shall be 50 parts per million. The product of the copper content and iron content, each expressed in parts per million, shall not exceed 125.

Total phosphorus. Shall be a minimum of 93 percent.

White phosphorus. Shall be a maximum of 0.01 percent.

Alumina. Shall be 2.5 ± 0.5 percent calculated as Al(OH)₃.

The phosphorus, red, stabilized powder shall be free flowing and free from lumps.


Phosphorus (White or Yellow, WP). $P_4$ (vapor), mw 123.92; colorless or yellowish, transparent, crys- solid, darkens on exposure to light; mp 44.1° (vap press 0.181 mm); bp 280° (vap d corresponds to formula $P_4$); d (solid, 20°) 1.82 g/cc, (liq, 44.5°) 1.745 g/cc. When exposed to air in the dark, emits a greenish light and gives off white fumes. Ignites at about 30° in moist air; the ignition temp is higher when the air is dry. Can be produced in an electric furnace from phosphate rock, sand and coke. The P vapor is driven off and condensed under w. Almost insol in w (1p in 300,000ps); v sl sol in abs alc (1g/400ml); sl sol in abs eth (1g/102ml); sol in chlf (1g/40ml); sol in benz (1g/35ml); v sol in CS₂ (1g/0.8ml) (Refs 5 & 6).

Ellern (Ref 4, pp 26-7 & 65-6) reports that Paracelsus (1490-1541), physician and philosopher on the nature of man and the origin of sickness, seems to have been the first to discover "the element of fire" in the residue of the pyrogenic decomposition of urine. More than a century later (1669), the alchemist Brandt discovered the waxy material that miraculously glowed without heat in the dark and that caught fire on the slightest provocation. After the latter accidental discovery, better methods of manufacture were found, but the material, at a price of 50 guineas per ounce, remained a mere curiosity until another hundred years had passed. In 1680 with the laborious manufacture of white phosphorus (WP) by Hankwets in London and the application by Robert Boyle of the then enormously expensive material to ignite a sulfur tipped wood splint, the story of its use in matches began. Between 1780 and 1830, numerous contrivances approaching the shape of an individual match were introduced, leading eventually, from about 1835 on, to real matches as we know them now. The poisonous qualities of WP matches showed themselves rarely in use except when the tips were chewed by children or swallowed by people wishing to commit suicide. Workers exposed during the manufacture of the matches to the fumes of WP, which entered the body mainly thru defective teeth, were subjected to an uncurable destruction of the jaw bones, the so-called phosphorus necrosis.

With the awakening of social conscience in the protection of workers, all civilized countries either eventually prohibited use of WP in matches or taxed them out of existence.

WP was largely used by the Allies in WWI for screening smokes in hand grenades and mortars. It was also suggested for use in incendiary bullets, and these proved to be very effective against $\text{H}_2\text{-filled aircraft}$, such as Zeppelins, used during WWI. During WWII it was also employed in incendiary and anti-personnel applications (Ref 1). More recent applications include the following. When scattered by the force of a burster charge, such as the Igniter AN-M9, the substance will easily ignite in air and, in turn ignite various fillings of incendiary bombs. Similarly, it will ignite when dispersed from items such as the WP Smoke Shell M302 for 60mm mortars, the M105 for 155mm howitzers, the WP Smoke Hand Grenade M15, or the Navy Smoke Bomb AN-M47A4 with either 100 lbs of WP or 74 lbs of plasticized WP (PWP—see below) (Ref 4, pp 26-7).

As indicated above, WP is widely used in
bursting-type munitions to produce smoke screens for ground-combat operations, and for signaling and spotting purposes. Slow-burning fragments of WP, produced and spread by an explosive burster, are incendiary while burning. Since burning WP produces flesh burns which are slow to heal, it is an excellent harassing agent.

WP is the most efficient smoke producer on a weight basis; however, the screening effectiveness of WP in bursting-type munitions is slight. Most of the charge burns within seconds following the burst, resulting in a smoke cone many times that required for effective screening. In addition, the temp rise in the cloud immediately surrounding the burst is sufficient to produce a strong thermal updraft which rapidly lifts the cloud from the ground so that the smoke cloud pillars. This may be helpful for signaling purposes but generally reduces the effectiveness of WP as a screening smoke. Two general ways to improve smoke-producing efficiency are possible. The first involves reduction of the heat of combustion, which can be accomplished only by using different P comnds. The second method, which is more attractive, involves controlling the rate of combustion by reducing the fragmentation of the WP. Several methods for controlling the fragmentation of WP have been tried, including the addition of mechanical reinforcement such as steel wool, asbestos, plastic tubes, wire screens, and other devices, causing ejection of the WP in pieces of predetermined size. Other methods attempted involved the alteration of the physical properties of WP so as to produce a plastic mass with low shattering characteristics (Ref 3).

Plasticized white phosphorus (PWP) was found to be the most promising development for control of the fragmentation of P and pillaring of the smoke. It consists of an intimate mix of granulated WP in a viscous rubber soln. The material burns more slowly and the particles do not disintegrate by melting. As a result, pillaring is reduced and the effective screening time is greatly prolonged. Test results have indicated that PWP produces distinctly better smoke screens than similar P-filled rounds. The anti-personnel incendiary action of PWP is as good as that of WP (Refs 3 & 4, p 149).

WP dissolves easily in carbon disulfide. If such a soln is soaked into filter paper or cotton cloth and exposed to air, the highly volatile solvent evaporates readily, and finely dispersed P residue bursts spontaneously into flame. Addition of gasoline or toluene to the P soln delays the spontaneous ignition because of slower evap rate of the added vehicles (Ref 4, p 27).

The spontaneous flaming of WP in air can also be made more reliable when a eutectic mixt of 55% WP with 45% phosphorus sesquisulfide (P4S3) is formed. This material (mp 40°, d 1.84g/cc) was used in WWII in one-shot flamethrowers designed to protect tanks against suicide attacks by infantry (E1 Antipersonnel Tank Protector) (Ref 4, p 27).

WP is considered a very dangerous expln and fire hazard, not only because of its spontaneous ignition in air, but because it can react vigorously with oxidizing materials. Ref 7 details documented instances of fire and/or explns with 100 different chemical comnds. Containers or amm confg WP should be kept below its mp (44.1°), as pressure may rupture the container. WP is preferably stored under w in sealed metal vessels enclosed in wooden boxes or metal drums. Use w to fight a WP fire (Ref 2, p 227).

WP is highly toxic with a lethal dose for man of less than 1mg/kg. High concns of the vapors evolved by burning are irritating to the nose, throat and lungs as well as the skin, eyes and mucous membranes. If P is ingested, it can be absorbed from the gastrointestinal tract or thru the lungs. The absorption of toxic quantities of P has an acute effect on the liver and is accompanied by vomiting and marked weakness. The long-continued absorption of small amts can result in necrosis of the mandible or jaw bone. Long-continued absorption, particularly thru the lungs, and thru the gastrointestinal tract can cause a chronic poisoning. This gives rise to a generalized form of weakness, attended by anemia, loss of appetite, gastrointestinal weakness and pallor. WP, when it comes into external contact with the eyes, can cause conjunctivitis (Refs 8 & 9).

No US Military Specification currently exists for WP.


**Phosphorus Oxychloride** (Phosphoryl chloride). POCls3, mw 153.35; colorless, clear, strongly fuming liq; pungent odor, mp 1.2°, bp 107.2°, d 1.67 g/cc, RI 1.460 (25/0). It is decomposed by w and alc with evolution of heat. Prepd from P tri- chloride, P pentoxide and chlorine (Refs 11 & 13)

P oxychloride and B triiodide react vigorously (Ref 2). The disposal of a benz soln of P oxychloride into a waste drum contg C disulfide and other solvents caused an instantaneous reaction, with the probable evolution of hydrogen chloride (Ref 6). Poor stirring during formualtion of 2,5- dimethylpyrrole with a preformed complex of dimethylformamide with P oxychloride caused eruption of flask contents. Reaction of the complex with a local excess of the pyrrole may have been involved (Ref 12). The interaction of P oxychloride and 2,6-dimethylpyridine n-oxide in the absence of a diluent caused an expbn (Ref 7). An expbn occurred immediately after pouring and capping of the P oxychloride recovered from the prep of ferrocene-1,1-dicarbonyl chloride. The storage bottle contained P oxychloride recovered from similar preps, which had been stored for about three months (Ref 5). Dimethyl sulf oxide decomps violently on contact with P oxychloride (Refs 3 & 8); gaseous Na reacts with luminescence at 270° (Ref 4). Zn dust ignites in contact with a little P oxychloride, and the subsequent addition of w liberates phosphine which ignites (Ref 1). When w reacts with P oxychloride there is little warning; first a little bubbling and then a rapid acceleration and pressure increase. Small quantities of P oxychloride were emptied into a scrap Ni drum contg about 28 lbs of w. After a delay of 15 to 30 minutes, the drum expld (Refs 9 & 10)

P oxychloride is highly toxic by inhalation and ingestion, and a strong irritant to skin and tissue (Refs 14 & 15)


**Phosphorus Pentachloride** (Phosphoric chloride, Phosphorus perchloride). PCl5, mw 208.27; white to pale yel, fuming, deliq, cryst mass; pungent, unpleasant odor; mp (under press) 148°; ordnarily sublimes without melting at 160–165°. Sol with decompn and liberation of much heat in w or alc; sol in C disulfide or tetrachloride. Can be prepd by the action of chlorine on P or P trichloride (Refs 9 & 10)

P pentachloride causes ignition on contact with Al powder (Ref 2), while contact with a mixt of chlorine and chlorine dioxide usually results in expbn, possibly due to formation of the more sensitive chlorine monoxide (Ref 5).

Interaction with diphosphorus trioxide is rather violent at ambient temp (Ref 3); treatment with fluorine causes the entire mass to become incandescent (Ref 1). Ignition occurs when hydroxylamine is mixed with P pentachloride (Ref 6), while mixts with Mg oxide react with brilliant incandescence (Ref 7). The residue from interaction of P pentachloride and nitride in benz and removal of solvent and phosphoryl chloride in vacuo expls violently on admission of air (Ref 12). A soln of P pentachloride in nitrobenzene is stable at 110°, but begins to de-
comp with accelerating violence above 120°, with evolution of nitrous fumes (Ref 13). A mixt with K produces a very violent expln on impact (Ref 8); molten Na can ignite or expld when in contact with P pentachloride (Ref 11). Interaction with w in limited quantities is violent, and the hydrolysis products may themselves react violently with more w (Ref 4).

P pentachloride is an irritant to skin and eyes; tolerance, 1 mg per cubic m of air (Refs 14 & 15).

Military specification MIL-P-51269, "Phosphorus Pentachloride, Analyzed Reagent" (14 May 1968) is mandatory for use by all Departments and Agencies of the Department of Defense. The chemical requirements are given below:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Maximum percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble matter</td>
<td>0.005</td>
</tr>
<tr>
<td>Residue after ignition</td>
<td>0.05</td>
</tr>
<tr>
<td>Sulfur compounds (as SO₄)</td>
<td>0.020</td>
</tr>
<tr>
<td>Heavy metals (as Pb)</td>
<td>0.002</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.002</td>
</tr>
</tbody>
</table>


**Phosphorus Pentoxide** (Phosphoric anhydride, phosphoric oxide, Diphosporus pentoxide). P₂O₅, mw 141.96; a soft, white powder; absorbs moisture from the air with avidity, forming meta-, para-, or orthophosphoric acid, depending upon amt of w absorbed and upon conditions of absorption; mp 580–585°, bp subl at 300°, d 2.387g/cc. Sol in w and alc with evolution of much heat and acrid white fumes. It is prep'd commercially by burning P in a current of dry air (Refs 5 & 8).

P pentoxide reacts violently with ammonia (Ref 4); with Ca oxide, Na hydroxide or Na carbonate when initiated by local heating (Ref 7); and with hydrogen fluoride at even 19.5° (Ref 6). A violent expln occurs if a soln of perchloric acid in chlf is poured on P pentoxide (Ref 1). Interaction with warm Na or K is incandescent, and is expld with heated Ca (Ref 2). Interaction with w is very energetic and highly exothermic. The increase in temp may be enough to ignite combustible materials if present and in contact (Ref 3).


**Phosphorus Trichloride** (Phosphoric chloride). PCl₃, mw 270.73; colorless, clear fuming liq, mp –111.8°, bp 76°, d 1.547g/cc. Decomps rapidly in moist air. Dissolves in w or alc with decomp and liberation of much heat. Sol in benz, chlf, eth and C disulfide. Prep'd by passing a current of dry chlorine over gently heated P, which ignites. The trichloride, admixed with some pentachloride, distills over. A small amt of P is added and the whole distilled (Refs 9 & 10).

P trichloride is highly toxic, and a strong irritant to skin and tissue. It is a dangerous fire risk in contact with w. Tolerance, 0.5ppm in air (Refs 12 & 13).

Several laboratory explns have occurred when using the reaction between P trichloride and acetic acid to form acetyl chloride. Poor heat control probably caused formation of phosphine (Ref 2). Two later explns may have been due to ingress of air and combustion of traces of phosphine (Ref 8). Al powder burns in P trichloride vapor (Ref 4); K ignites and molten Na explds on contact (Ref 3). Each drop of chromyl chloride added to well-cooled P trichloride produces a hissing noise, incandescence, and sometimes an expln (Ref 5). It reacts with fluorine with incandescence (Ref 1), and with ignition...
when mixed with hydroxylamine (Ref 6). An expln occurs when P trichloride is brought in contact with nitric or nitrous acid (Ref 7). Its reaction with w is exothermic and immediately violent, and is accompanied by liberation of some diphosphane which ignites (Ref 11).

The requirements of the US Armed Forces for P trichloride are covered in two specifications, MIL-P-10398B (11 Feb 1969) for Phosphorus Trichloride, Technical, and MIL-P-51300 (12 March 1969) for Phosphorus Trichloride, Analyzed Reagent.

MIL-P-10398B contains the following requirements for physical characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>1.582</td>
<td>1.588</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>15.5/15.5°C</td>
<td></td>
</tr>
<tr>
<td>Distillation range (°C):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial boiling point</td>
<td>74.5</td>
<td>—</td>
</tr>
<tr>
<td>Dry point</td>
<td>—</td>
<td>79.0</td>
</tr>
<tr>
<td>Total range</td>
<td>—</td>
<td>3.0</td>
</tr>
</tbody>
</table>

MIL-P-51300 contains the following requirements for physical and chemical characteristics:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.54</td>
<td>1.60</td>
</tr>
<tr>
<td>Boiling range, °C</td>
<td>75.0</td>
<td>76.0</td>
</tr>
<tr>
<td>Sulfate (SO₄), percent</td>
<td>—</td>
<td>To pass test</td>
</tr>
<tr>
<td>Metals (as Pb), percent</td>
<td>—</td>
<td>0.001</td>
</tr>
<tr>
<td>Iron (Fe), percent</td>
<td>—</td>
<td>0.0015</td>
</tr>
<tr>
<td>by weight</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>


Phosphorous Trioxide (Diphosphorus trioxide). P₂O₃, mw 109.95, transparent monoclinic crystals, mp 23.8°, bp 173.1° in nitrogen atm, d 2.135 g/cc. Exists as P₄O₁₀ when in vapor phase or in benz soln. Disproportionates into red P and P₂O₃ when heated above 210°. Sol in benz and C disulfide. When placed in cold w, H₃PO₃ is formed. Prepd by treating PCl₃ with tetramethylammonium sulfate in liq SO₂, or from the elements (Ref 6). It is highly toxic (Ref 7).

The interaction of ammonia and molten P trioxide under nitrogen is rather violent, and the mixt ignites (Ref 2). Its interaction with disulphur dichloride is very violent (Ref 5); it ignites in contact with excess chlorine gas, and reacts violently, usually igniting, with liq bromine (Ref 2). Interaction with air or oxygen is rapid and, at slightly elevated temps in air or at high oxygen concn, ignition is very probable, particularly if the P trioxide is molten or distributed as a thin layer. The solid in contact with oxygen at 50–60° instantly ignites with a flame of almost blinding brilliance (Ref 3). The reaction between P trioxide and P pentachloride is violent at ordinary temps (Ref 1); sulfur monoxide reacts with great violence (Ref 2). Interaction of a mixt of S and P trioxide under inert atm above 160° to form P oxytsulfide is violent on anything but a small scale (Ref 2).

The addition of sulfuric acid to P trioxide causes violent oxidation, and ignition if more than 1–2g is used (Ref 5). Its reaction with cold w is slow, but with hot w, violent, the evolved phosphine igniting. With more than 2g of P trioxide, violent explns occur (Ref 4).

Photochemistry of Explosives. The addition of radiant energy to a chemical system produces electronically excited molecules that are capable of undergoing chemical reactions. An organic molecule in which all the electrons are in stable orbitals is said to be in the ground electronic state. These orbitals may be either bonding or nonbonding. If a photon of the proper energy collides with the molecule, i.e., the photon is absorbed, one of the electrons is promoted (excited) to an unoccupied orbital of higher energy—a nonbonding molecular orbital. Electronic excitation results in spatial redistribution of the valence electrons with concomitant changes in internuclear configurations. Since chemical reactions are controlled to a great extent by these factors, an electronically excited molecule undergoes chemical reactions that may be distinctly different from those of its ground-state counterpart.

The energy of the photon is defined in terms of its frequency or wavelength:

\[ E = h\nu = hc/\lambda \]

where \( E \) is energy; \( h \) is Planck’s constant (6.6\times10^{-27}\text{erg-sec})\;\nu \) is the frequency of the radiation (sec^{-1})\; c \) is the speed of light; and \( \lambda \) is the wavelength of the radiation. When a photon is absorbed, all of its energy is imparted to the absorbing species. The primary act following absorption depends on the wavelength of the incident light. Photochemistry studies photons whose energies lie in the ultraviolet region (1000–4000 Å) and in the visible region (4000–7000 Å) of the electromagnetic spectrum; such photons are primarily a cause of electronically excited molecules. When this energy is released as chemical energy, fragmentation, free-radical formation, isomerization, and addition reactions may take place (Ref 6).

Many photochemical studies have been conducted over the past 40 years on materials of ordnance interest. The major studies are annotated below in chronological sequence:

Schultz and Ganguly, in 1925, noted that the surface of pulverized TNT became colored on exposure to sunlight. They concluded that tautomeric quinoxalines were formed thru an unstable intermediate. In acetone, a stable intermediate formed (Ref 1). Gray, Bonomo and Denner (Ref 8) could not repeat their results. Leighton and Lucy studied o-nitrobenzaldehyde, 2,4-dinitrobenzaldehyde and 2,4,6-trinitrobenzaldehyde as solids and in acet and lignin soln, on exposure to radiation between 2654–4040 Å. For o-nitrobenzaldehyde, quantum yield was independent of wavelength, oxygen and state. The product was o-nitrosobenzoin acid (Ref 2).

Shelegova irradiated nitrobenzene vapor with various light sources. In the 2160–2900 Å region the products were phenol and NO\sb{2}; in the 1850–2160 Å region, phenol and polynitrobenzenes (Ref 3).

Gorislavets (Ref 4) claimed that the nitration of benzene or nitrobenzene with nitrogen dioxide readily occurred on irradiation with rays of certain definite wavelengths which activate NO\sb{2}. Thus, benzene was nitrated quantitatively at 4000–7000 Å at a temp of 55–60°. The highest yield of dinitrobenzene was obtained at 1800–2900 Å. These results were not confirmed by Hastings and Matsen (Ref 5) who reported nitrosobenzene and p-nitrophenol as the main products from the mercury arc irradiation of nitrobenzene vapor. They concluded that the absorption led to the release of an O atom from the NO\sb{2} group which inserted itself in the parent molecule.

Lippert and Vogel (Ref 7) asserted, on the other hand, that on irradiation with high intensity ultra-violet light, nitrocompds undergo dissociation into free radicals:

\[ \text{ArNO}_2 \rightarrow \text{Ar.} + \cdot \text{NO}_2 \]

Marguriet et al. (Ref 9) photolyzed solns of aromatic nitrocompds in 95% alc using an unfiltered 400 watt mercury lamp. No compd was found to be phototropic which did not have a nitrogroup ortho to a benzyl hydrogen. They hypothesized that an intramolecular process involving an H-atom transfer was operative.

Wettermark (Ref 10, 11 & 12) studied o-nitrotoluene and dinitrotoluene, flash photolysed in w and alc. He observed transients, and noted that the absorption spectra was a function of pH. He concluded that intramolecular Hatom transfer was involved.

Tench and Coppens (Ref 13) photolyzed o-nitrobenzaldehyde, nitrobenzene, and nitrobenzoic acid with light > 3500 Å. ESR measurements revealed the presence of radicals for o-nitrobenzaldehyde (in solns and powder), with no radicals observed with nitrobenzene and
E. S. S. Smith, P. J. Bodine, and H. H. Schröder (Ref 12) noted that the nitrobenzyl group is an effective electron-withdrawing group and that it can be used to increase the quantum yield of radical formation in photochemical reactions.

Ward (Ref 15) and Brown and Williams (Ref 16) studied nitrobenzene with radiation > 3300 Å using tetrahydrofuran (THF) as solvent in degassed solns. The effects of low temp were also studied. An ESR signal, attributed to the C₆H₅N(O₂)H radical, was obtained with THF as solvent. No ESR signal was obtained when perfluoronaphthalene was added. They concluded that the triplet state of nitrobenzene was an intermediate.

B. Suryanarayana, J.R. Autéa, and R.J. Graybush (Ref 16a), during a study of solid phase transitions in the four polymorphic forms of HMX utilizing differential thermal analysis (DTA) techniques, found that prior irradiation with 2537 Å light caused the β to β' transformation to occur approximately 15° below the transition point of unirradiated material. A similar but smaller effect, a decrease of 5°, was observed after irradiation of β-HMX with 3100–3400 Å light. They hypothesized the involvement of a free radical or a trapped charge.

Hurley and Testa (Ref 17) exposed nitrobenzene in isopropyl alcohol, degassed and in air, to a mercury lamp at 3660 Å. Products in the absence of air were acetone and phenylhydroxylamine (PHA). In air PHA was oxidized to nitrosobenzene which couples with PHA to form azyoxynitrobenzene. They hypothesized that the triplet molecule abstracted H-atoms from the solvent; no effect was noted with benzene as solvent. They also worked with nitrobenzene in isopropyl alcohol-water mixts containing HCl with a mercury lamp at 3660 Å (Ref 18), and found that the quantum yields depended on pH and isopropyl alcohol content, but were independent of oxygen with acid present. Their conclusion was that the quantum yield consisted of two parts, H abstraction by the triplet, and protonation of the triplet.

Strom and Weinstein (Ref 19) used an unfiltered 200 watt mercury lamp on degassed solns of o-nitrocumarine and o-nitrotoluene. The former yielded radicals, while with the latter the yield was markedly lower. The radicals were stable for days and could also be formed in the presence of oxygen. No radicals were formed with corresponding parahydrogenated compds. It was thought that the reaction proceeded via an intramolecular step.

Ballop and Bunc (Ref 20) employed a variety of radiation wavelengths, nitrocompds and solvents. For wavelengths less than 2900 Å, aniline was the main product, while above 2900 Å, bimolecular species such as azobenzene predominated. Since oxygen had little effect on aniline production, expts were performed in the presence of oxygen. For nitrobenzene in isopropyl alcohol, no azyoxynitrobenzene was produced as with Hurley and Testa (See above Ref 17). They concluded that the excited state abstracts H-atoms, and suggest that the nitrobenzene triplet is in π, π*, and that nitrosobenzene is an unobserved intermediate.

Hashimoto, Sunamoto, Fujii, and Kano (Ref 21) used a 130 watt mercury lamp to irradiate isopropyl alcohol-HCl-nitrocompd solns. The effect of oxygen was also studied. They found that in the absence of HCl, nitrobenzene produced phenylhydroxylamine. When HCl was present, it produced aniline and other products. No explanation of mechanism was given.

Weller and Hamilton (Ref 22) irradiated solns of nitrobenzene and alkanes with a 450 watt mercury lamp using different glass filters. Good yields of alcohols and carbonyl compds were observed. They concluded that the oxidation involved an H-atom abstraction by nitrobenzene.

Ayscough, Sealy and Woods (Ref 23) irradiated nitrosobenzene and nitrobenzenone in isopropyl alcohol and other solvents with an incident wavelength greater than 3000 Å, and performed ESR studies on the solns. They found a stable radical, C₆H₅N(NO), and concluded that participation of a triplet state was not involved with nitrocompds, and not firmly established with nitrocompds.

Sandus and Slagg (Ref 24) performed flash and continuous photolysis expts at 2537 Å (π → π* transitions) on nitrocompds in soln. Flash photolysis revealed intermediates for o-nitrotoluene and its nitroderivatives. The
spectrum and mean lifetime of the intermediate for flashed TNT were detd. Continuous photolysis extps revealed that all the aromatic nitrocompds had disappearance quantum yields of the order of 10⁻³, implying that the most important reaction occurring was the deactivation to the ground state of the original molecule. The presence or absence of oxygen did not appear to be significant. Product analyses suggested that aromatic nitrosocompds and nitrophenols were the main products. However, the observed products did not conform in a simple manner to the constraints of the isosbestic points observed in all the photolyses. It appeared that other products were present, some of which could have low extinction coeffs in the spectral range studied.

The photolysis of solid dimethylnitramine with 2537Å light resulted in the formation of dimethylnitrosamine as a major product (Ref 25). The mechanism of bond-breaking was investigated via a ¹⁵N tracer technique, and showed that the nitrosamine arose from the nitramine as a result of an N-O bond cleavage, and that the nitrosamine after being formed underwent an almost 100% light-induced rearrangement involving the bond between the two N-atoms.

Nanosecond flash photolysis studies of α-nitronaphthalene in polar and nonpolar solvents led to the detection of the triplet-triplet absorption spectrum of this nitrocompd (Ref 26). A large red shift observed in polar solvents was indicative of the intramolecular charge transfer character of the triplet state. The charge of the dipole moment accompanying the transition T₁ → T₃, as well as rate constants for electron and proton transfer reactions involving the T₁ state of α-nitronaphthalene, were determined. The lower reactivity in polar solvents was attributed to a reduced n-π* and increased charge transfer character of the triplet state.

The flash photolysis of 2,4,6-trinitrotoluene (TNT) aerated solns in alcohols generated a transient species with absorption maxima at 430 and 510nm (Ref 27). The yield of the transient was a function of oxygen concn, and its rate of formation was viscosity dependent. In deaerated solns, instead of the transient, a brown permanent product, identified as a charge transfer (CT) complex with absorption maxima at 470 and 550nm, was produced. These species were formed only in polar solvents with relatively high proton affinity. The data suggested an intermolecular proton transfer, from electronically excited TNB to the solvent forming the anion

\[
\text{NO}_2\text{C}\cdots\text{O}_2^-(\text{TNB}^\cdots\text{O}_2^\cdots)
\]

The anion thereby produced interacts with oxygen in aerated alcohols to form the transient attributed to CT complex

\[
\text{NO}_2\text{C}\cdots\text{O}_2(\text{TNB}^\cdots\text{O}_2)
\]

while in deaerated alcohols the anion reacted with the solvent to produce RO⁻, which led to the CT complex RO⁻TNB

Capellos and Suryanarayanan (Ref 28) described a ruby laser nanosecond flash photolysis system to study the chemical reactivity of electronically excited state of aromatic nitrocompds. The system was capable of recording absorption spectra of transient species with half-lives in the range of 20 nanoseconds (20 x 10⁻⁹ sec) to 1 millisecond (10⁻³ sec). Kinetic data pertaining to the lifetime of electronically excited states could be recorded by following the transient absorption as a function of time. Preliminary data on the spectroscopic and kinetic behavior of 1,4-dinitronaphthalene triplet excited state were obtained with this equipment.

The flash photolysis of 2,4,6-trinitrotoluene solns (TNT) indicated a photochemically induced isomerization leading to the aci-quinoid isomer

\[
\text{CH}_2\text{NO}_2
\]

with an absorption maximum at 460nm in nonpolar solvents, or the conjugate base...
of the aci-quinoid isomer with absorption maxima at 500, 540, and 630nm in polar solvents. Both species, the quinoid isomer and the conjugate base, had transient existence and their identification was based on detailed spectroscopic and kinetic studies. The magnitude of the negative charge on the transient conjugate base was deth with salt effect expts and found to be equal to unity (Ref 27).

Nanosecond flash photolysis of 1,4-dinitronaphthalene in nonpolar and polar solvents showed a transient species with maximum absorption and lifetime dependent on solvent polarity. In deaerated n-hexane the absorption maximum and lifetime were 425nm and 530ns, while in deaerated ethanol the corresponding values were 470nm and 1.7μsec. This transient absorption was attributed to the triplet excited state of 1,4-nitronaphthalene, and the observed red shift as well as its longer lifetime in polar solvents were considered to be indicative of the intramolecular charge transfer character of this state. The change of dipole moment accompanying the transition T₁ → T₂, as well as rate constants for electron and proton transfer reactions involving the T₁ state of 1,4-dinitronaphthalene were deth. Spectroscopic and kinetic data obtained indicated that the triplet state of 1,4-nitronaphthalene behaved like a n→π* state in nonpolar media, while in polar solvents the n→π* character of the state was reduced with a simultaneous increase in the charge transfer character (Ref 30).


Photoflash Compositions. See under Pyrotechnics, Military in this Vol


PH-Salz (PH-Salt). Ger designation for Ethylene-diamine Dinitrate (EDD, EDDN, EDAD or DIAIMIN). See in Vol 6, E236-L to E237-R

In Ger, PH-Salz was prep by treating ethylenedichloride with ammonia and Na hydroxide, followed by nitration with nitric acid not stronger than 50%. Although PH-Salz has a high mp (185 °C), it has the property of depressing the mp of other high mp compds. For this reason, the Germans used it to obtain castable expl mixts during WWII. For example, a mixt of 45% PH-Salz and 55% AN melts at 105 °C and can be cast-loaded. Such a mixt has an exp power equal to that of TNT or Amatol, but has the disadvantage of shrinking considerably on cooling. The addition of an Ca nitrate to this mixt practically eliminates shrinkage and results in a very good cast. The following mixts contg PH-Salz were used for filling shells as a substitute for TNT:

Ammonit. AN 46, PH-Salz 46 & Ca(NO₃)₂. 4H₂O (tech) 8%; d of fragments 39–40m (see Fragment Concentration Test in Vol 3, D64-L)

Ammonit. AN 55, PH-Salz 10, Ca(NO₃)₂. 4H₂O 10, RDX 20 & Na nitrate 5%; d 1.53g/cc; casting temp 108 °C, d of fragments 40m (Ref 3)

H-5 (Ammonit). AN 50, PH-Salz 10, Ca(NO₃)₂. 4H₂O 15 & RDX 20% (Ref 2)

S-16. AN 32, PH-Salz 10, Na nitrate 6 or 8, K nitrate 2 or 0 & Al powder 40% (Ref 2)

S-22 (Hexa). AN 45, PH-Salz 14, Na nitrate 9, K nitrate 3, RDX 14 & Al powder 15% (Ref 2)

S-22 (Hexa). AN 45, PH-Salz 14, Na nitrate 9, K nitrate 3, HNDPhA 14 & Al powder 15% (Ref 2)

Amatol 41. AN 52, PH-Salz 30, Ca(NO₃)₂. 4H₂O 6, RDX 10 & Montan wax 2% (Ref 3)

Compns contg Al were particularly suitable for underwater ordnance because they possessed high blast effect. PH-Salz could also be used straight or slightly phlegmatized. In the latter case, it was particularly suitable for use in anti-concrete shells, called Be-Granate (Be is an abbreviation for Beton = concrete)

Refs: 1) PB (Publication Board of the US Office of Technical Services) Rept No 925 (1945), 24 2) PB Rept No 1820, 29 3) PBL Rept No 85–160 (1946), 23 4) B.T. Fedoroff et al, PATR 2510, Ger 131–2 (1958)

Phthalic Acids and Derivatives

C₆H₄(COOH)₂, mw 166.13

o-Phthalic Acid (Phthalic Acid, Benzoldicarbonsäure-(1,2) in Ger). Monod crystals, mp 191 °C, d 1.593 g/cc at 20/°C. Prepn & other properties given in Beil 8, 791–8, (349–50) & [580–84]

m-Phthalic Acid (Isophthalic Acid, Benzoldicarbonsäure-(1,3) in Ger). Needles from hot w or alc, mp 347–8 °C, bp sublimes. Prepn & other properties given in Beil 9, 832–4, (371) & [608–9]

p-Phthalic Acid (Terephthalic Acid, Benzoldicarbonsäure-(1,4) in Ger). Cryst or amorph powder, mp 425 °C (starts to sublime above 300 °C). Prepn & other properties given in Beil 9, 841–3, (373–4) & [611–12]

Note: The exothermic nitration of phthalic acid or phthalic anhydride by a fuming nitric acid-sulfuric acid mixt may give mixts of the potentially expl phthaloyl nitrates or nitriles or their nitro derivatives. Formation of these compds can be avoided if the nitrating mixt is
extensively diluted with sulfuric acid and if a small (1.5 mole equiv) of nitric acid is present (Anon, Chem&Ind 17, 664 (1972); Ibid 20, 790 (1972))

Mononitrophthalic Acids
\[ O_2N.C_6H_4(COOH)_2, \text{ mw } 211.13, \text{ N } 6.63\%

3-Nitro-o-phthalic Acid. Pale yel prisms or plates from w; mp dec 207–230°. Prepn and properties are given in Refs
Refs: 1) Beil 9, 823–4, (367) & [605]
2) O. Miller, Ann 208, 240 (1881) 3) F.C. Whitmore, Ed, OrgSynth 7 (1927), 70

It forms salts, some of which are expl, eg:
Basic Lead Salt, PbC_6H_4O_7N, mw 416.32, N 3.36%. Insol in w. For prepn and properties, see Ref 2. Was proposed by Brün for use as a component of ammo priming mixts (Ref 3)
Refs: 1) Beil 9, 825 2) A. Faust, Ann 160, 57–59 (1871) 3) W. Brün, USP 1971030 (1934) & CA 28, 6314 (1934)

Silver Salt, Ag_3C_6H_4O_7N. Insol in w; puffs off on heating. Prepn and properties are given in Ref 2
Refs: 1) Beil 9, 825 2) A. Laurent, Ann 41, 112 (1842)

4-Nitro-o-phthalic Acid. Needles from eth, mp 162–64°. Easily sol in w & alc; sol in hot AcOH; diff sol in cold AcOH; fairly sol in eth; insol in chlf, benz, petr eth & C tetrachloride. Prepn and properties are given in Refs

It forms salts, some of which are expl, eg:
Basic Lead Salt, PbC_6H_4O_7N, mw 416.32, N 3.36%. Was proposed by Brün for use in mixts with Pb Styphnate, Pb nitrate, etc, in expl comps (Ref 3)

Its potassium salt was reported to be a mild expl (Ref 2), as are probably its silver and barium salts

2-Nitro-m-phthalic Acid. Prisms from methanol, mp 310–315° (begins to brown ca 287°). Sl sol in w, easily sol in alc or eth. Its barium salt, which is very sol in w, is probably expl (Ref 2)
Refs: 1) Beil 9, 839, (373) & [610] 2) E. Noelting & C. Grachot, Ber 39, 73 (1906)
3) C.W. James et al, JCS 117, 774 (1920)

4-Nitro-m-phthalic Acid. Crysts, mp 255–60°. Diff sol in cold w, v sol in hot w, alc & eth. Forms numerous salts of which the silver salt was reported to be expl
Ref: Beil 9, 839, (373) & [610]

5-Nitro-m-phthalic Acid. Colorl crysts from alc, mp 255–56°. V sol in alc, eth or hot w; sl sol in cold w. Forms numerous salts of which the silver salt was reported to be expl
Ref: Beil 9, 839–40 & (373)

2-Nitro-p-phthalic Acid (Nitroteterephthalic Acid). Only one isomer is possible. Crysts, mp 268–70°. Easily sol in alc or eth, sol in hot w. Can be prepd by nitration of terephthalic acid or by other methods given in the Refs. Some of its salts are probably expl

Dinitrophthalic Acids
\[ (O_2N)_2C_6H_4(COOH)_2, \text{ mw } 256.14, \text{ N } 10.94\%

3,5-Dinitro-o-phthalic Acid. Prisms from eth, mp 225–6°. Very sol in w, alc & eth; insol in ligcr, C disulfide and benz. Can be prepd by the oxidation of 5,7-dinitro-1,2,3,4-tetrahydro-naphthalene with 30% boiling nitric acid or by other methods given in the Refs. The barium salt, C_6H_2(NO_2)_4, Ba is expl
3.6-Dinitro-o-phthalic Acid. Needles from eth, mp 200–202°. Easily sol in w, alc or eth. Can be prepd by heating 1,5-dinitronaphthalene with mixed nitric-sulfuric acid. Its barium salt (Refs 2 & 3) is expl

Refs: 1) Beil 9, 831–2 2) V. Merz & W. Weth, Ber 15, 2725 (1882) 3) W. Will, Ber 28, 369 (1895)

2.5 (or 4.5) Dinitro-m-phthalic Acid. Crystals from w with 5H₂O; loses it when heated to 100°; mp 215°. Si sol in w, sol in alc, nearly insol in eth. Can be prepd by heating 1 p of isophthalic acid with 5p of fuming nitric acid in a sealed tube at 150–180° for 6 hrs. Forms salts, some of which (silver salt) are expl


2.3-Dinitro-p-phthalic Acid (2,3-Dinitrotetraphthalic Acid). Glassy crystals from hot w; mp > 290° with decomp; expls on rapid heating. Can be prepd by treating 2,3-dinitro-p-tolyllic acid with concd nitric acid in a sealed tube at 170°

Refs: 1) Beil 9, 853 2) C. Haeussermann & E. Martz, Ber 26, 2982–85 (1893)

2.5-Dinitro-p-phthalic Acid (2,5-Dinitrotetraphthalic Acid). Prisms from w; mp > 280° with decomp; expls when heated rapidly. Sol in w. Can be prepd by heating 2,5-dinitro-p-phthalic acid with concd nitric acid in a sealed tube at 140°. Forms expl salts such as BaC₄H₃O₈N₂

Refs: 1) Beil 9, 853 2) C. Haeussermann & E. Martz, Ber 26, 2984 (1893)

2.6-Dinitro-p-phthalic Acid (2,6-Dinitrotetraphthalic Acid). Crystals from hot w; mp ca 255° with decomp; expls on rapid heating. Difficultly sol in w. Can be prepd by treating p-phthalic acid with mixed nitric-sulfuric acid, or by heating 2,6-dinitro-p-cymol with fuming nitric acid in a closed tube at 140°. Forms an expl barium salt

Refs: 1) Beil 9, 853 & [615] 2) C. Haeussermann & E. Martz, Ber 26, 2983 (1893) 3) A.S. Wheeler & C.R. Harris, JACS 49, 497 (1927)

2,4,6-Trinitro-m-phthalic Acid (2,4,6-Trinitroisophthalic Acid). (O₃N₃)₂C₆H(COOH)₂, mw 301.14, N 13.96%. Crystals from w, mp 196–7° with decomp. Can be prepd by oxidation of 2,4,6-trinitro-m-xylene with chromium oxide in concd sulfuric acid at 80–90°. Its silver salt, yel crys, expls on heating

Refs: 1) Beil 9, [611] 2) M. Giua, Gazz 52 (I), 186 (1922); JCS 122 (I), 534 (1922)

Phthalic Acids — Azides and Diazides

3-Nitrophthalic Acid Azide [3-Nitrophthalic Acid Azide (1), in Ger]. HO₂C.C₆H₃(NO₂).CO.N₃, mw 236.16, N 23.73%. Scales from eth & petr eth, mp expls on heating. Can be prepd by treating the hydrazide of 3-nitrophthalic acid with nitrous acid under cooling conditions

Refs: 1) Beil 9, (370) 2) T. Curtius & A. Semper, Ber 46, 1162 & 1167 (1913)

Isophthalic Acid Diazide (m-Phthalic Acid Diazone). C₆H₄(CO.N₃)₂, mw 216.18, N 38.88%. Prisms from acet, mp 56°, expls on further heating. Easily sol in acet or eth. Can be prepd by treating isophthalic acid hydrazide hydrochloride with Na nitrite in cold aq soln


Terephthalic Acid Diazide. C₆H₄(CO.N₃)₂, mw 216.18, N 38.88%. Plates from acet, mp 110°, expls on further heating. Easily sol in eth or acet. Can be prepd by treating terephthalic acid hydrazide hydrochloride with Na nitrite in cold aq soln

Refs: 1) Beil 9, 847 & (376) 2) E. Davvidis, JPrChem [2], 54, 84 (1896)
Phthalic Anhydride. $C_8H_4O_3$, mw 148.11, white crystalline needles, mp 131.16°C, bp 285°C, sublimes below bp, flash pt 152°C, combustible, auto-ignition temp 584°C, flammable limits 1.7–10.5%.

Sol in alc, sl sol in eth and hot w. Prepd by the catalytic oxidn of naphthalene or ortho-xylene.

Attempts to follow a published method for the nitration of phthalic anhydride in sulfuric acid at 80–100°C with fuming nitric acid caused an eruptive decomp to occur after a 2 hr delay (Ref 3). It was found that this hazard could be eliminated thru use of a smaller excess of nitric acid at 55–65°C (Ref 4). Possible causes of the delayed eruption were suggested as the formation of potentially expl mixts of phthaloyl nitrates or nitrites, or their nitro derivatives.


Phthalide (Isobenzofuranone, 1-Phthalanone, 1-Oxo-phthalan in Ger). $C_8H_4O_2$, mw 134.13, needles from w, mp 73°C (65°C), bp 290°C, d 1.164 g/cc at 99/4°C, Qc 6470 cal/g, Qf 653 cal/g, Qp 671 cal/g. V sol in w, sol in alc. Can be prepd by reducing phthalimide, $C_6H_4(CO)_{2}NH$, with Zn dust in acq Na hydroxide or by other methods (Ref 1). It was proposed by Parodi-Delfino et al. as a gelatinizer and stabilizer for NC in smokeless powd. It was claimed that in double-base propnt, it was superior to Centralite (Ref 2). Allison (Ref 3) used it as a deterrent for coating propnt grains.

Refs: 1) Beil 17, 310, (161) & [332] 2) L. Parodi-Delfino et al., CongrInternQuimPuraAplicada 4, 447 (1934) & CA 30, 3237 (1936); USP 1609303 (1926) & CA 21, 325 (1927) 3) E.R. Allison, USP 2267261 (1941) & CA 36, 2725 (1942) 4) P. Tavernier, MP 38, 308 & 329 (1956)

Phthalide forms an expl diazide:

3,3-Diazidophthalide. $C_8H_4N_2O_2$, mw 216.18, N 38.9%, mp 56°C (decomp), detonates when heated rapidly. Can be prepd from phthalyl chloride and Na azide in acq acet under cold conditions.


Phthaloylperoxide (Phthalylsuperoxid in Ger). $(C_8H_4O_4)_x$, mw (164.12)x, crys, mp 133.5°C with decmp, puffs off at about 136°C. Insol in the usual organic solvents. Was prepd by von Pechmann and Vanino by shaking phthalylchloride with a soln of Na peroxide in 10% acq Na acetate under cooling. Explodes on rapid heating or when brought into contact with concd sulfuric acid.

Refs: 1) Beil 9, 804 2) H. von Pechmann & L. Vanino, Ber 27, 1511–12 (1894)

PHX. Code letters for 1-Acetoxyxylmeth-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane. See Vol 1, A52-L.

PIAT. Acronym for projector infantry antitank. A Brit WWII weapon based on the shaped charge effect. It fired a rocket-propelled charge weighing 3 lbs which could pierce 4-inch armor plate.


Picarmit. A plastic military Dynamite, developed at PicArsn about 1949, contg 70 RDX, 15 t alc, 9 di(2-ethylhexyl) sebacate, 3 polyisobutylene, and 3% SAE 10 motor oil. It had a wt strength equivalent to 47% straight Dynamite, a rate of detonation of 6625 m/sec at its max d of 1.40 g/cc when initiated with a Corps of Engineers Special Blasting Cap, and a brsance at the above d that was 1/3 to 1/2 that of Composition C-3 (see Vol 3, C484-R). It had the consistency of bread dough, was plastic at −70°F and remained flexible below this temp, was odorless, non-toxic, non-tacky, stable in
storage at 170°F, w-resistant, non-hygroscopic, and could be furnished in any color desired for camouflage purposes. It was superseded in 1950 by Composition C-4, also called Harrisite (see Vol 3, C485)

Ref: K.G. Ottoson, "Development of Military Explosives Equivalent to Commercial Dyna-mites", PATR 1760 (1950)

Picatinny Arsenal. A US Army Armament Command (USAAAMCOM) installation located near Dover, Morris County, New Jersey

USAAAMCOM Regulation 10-10 assigns Picatinny Arsenal its mission, major functions and materiel assignments within the Armament Command. The following is an extract from that regulation:

**Mission.** To perform research, design development, engineering, integrated logistic support, maintenance support, procurement, fabrication, and product assurance of assigned materiel.

**Major Functions.**

1. Conduct research, development, test and evaluation with respect to assigned materiel and perform specialized research and technology in the following fields:
   a. Energetic materials
   b. Safing, arming, and fuzing
   c. Nuclear weapons
   d. Non-metallic materials excluding rubber, greases, lubricants, corrosion preventatives and fuels
   e. Munitions/Ammunition

2. Conduct exploratory and engineering activities in the methods and technology of manufacture as applied to assigned commodities and their components, materials and ancillary equipment except projectile metal parts which are the responsibility of Frankford Arsenal, and specified elements of chemical items which are the responsibility of Edgewood Arsenal. This is to include support of plant/facilities modernization within ARLCOM, abatement of environmental contamination caused by manufacturing processes and exploitation of automation techniques.

3. Perform total system safety management throughout life cycle of all assigned systems, subsystems and equipment.

4. Perform in-house fabrication and pilot plant manufacture of prototypes and preproduction evaluation quantities; and emergency production of limited quantities of assigned critical items to fill in supply gap until industry can meet needs.

5. Conduct exploratory development for packaging of munitions which are assigned to ARMCOM.

6. Perform cataloging, standardization, new equipment training, and design of training devices, and provide technical assistance to users, as required by HQ, ARMCOM.

7. Perform design, product, process, maintenance, and value engineering, and related product assurance for assigned material.

8. Perform mobilization planning (general mobilization, continuity of operations, and industrial preparedness) to include utilization of pilot line fabrication and shop capabilities to provide assigned materiel in short supply until such time as industry can assure quantity production.

9. Develop, publish, and maintain supporting emergency plans in accordance with AMC guidance and the ARMCOM Civil Disturbance, Force Mobilization, War Emergency, and Disaster Control Plans.


11. Execute the technical management of the ARMCOM Weapons Vulnerability Program including Penetration Aids.

12. Provide technical support to the Federal Bureau of Investigation for operation and maintenance of the National Bomb Data Center.

13. Provide technical support to, and membership in, the Army Nuclear Weapons System Safety Committee.

14. Perform, as directed, maintenance and repair on nuclear weapons, radar, and inertial fuzes, Permissive Action Link Devices, ADM Firing Systems, and Adaptation Kits.

15. Operate the Department of the Army repository of drawing information pertaining to nuclear components received from the Atomic Energy Commission and its contractors.

16. Operate technical activity in support of DA hazardous munitions countermeasures program and technical escort program including explosives ordnance disposal (EOD) for all items assigned to the Army, including foreign surface munitions.
Perform surveillance testing on all standard US Army gun propellant and rocket propellants to support and advise field surveillance activities of the safe life potential and/or possible degradation of both bulk stored material and items using these propellants.

Provide guidance and assistance to the Navy and Air Force relative to Army requirements for EOD technical publications and tools and equipment developed and maintained by those services, and to be used by Army EOD units. Operate the US Army Technical Detachment.

Provide national procurement of nuclear munitions and of selected non-nuclear commodities as assigned.

Develop, prepare, and publish demilitarization procedures for assigned material.

Perform malfunction/deficiency investigations for assigned material.

Maintain direct contact with users to monitor design engineering and quality assurance potential problems for newly fielded items.

Material Assignments.

1. Nuclear and non-nuclear munitions (to include mines, grenades, demolition devices, explosives, explosive devices and initiators) except chemical and smoke munitions assigned to Edgewood Arsenal.

2. Artillery and tank ammunition (nuclear and non-nuclear).

3. Recoilless rifle ammunition including rocket assisted types.

4. Aircraft dispersed munitions except for chemical items assigned to Edgewood Arsenal.

5. Nuclear and non-nuclear rocket and missile warhead sections, and assigned rocket motors.

6. Propellants and pyrotechnics, less smoke and tracers.

7. Safing and arming devices and fuzes except proximity and those assigned to Frankford Arsenal.

8. Non-metallic cartridge cases.

9. Other assigned equipment pertinent to mission items.

The Arsenal is located in the central portion of northern New Jersey, near the town of Dover. This places it at the outer rim of the New York metropolitan area. It occupies a ten mile long valley, lying between mountain ridges which serve as natural barricades. The valley also has a natural water supply which, even today, is adequate. These are the three attributes for which the site was selected: nearness to the world of commerce, means of protection of the surrounding area from the hazards inherent in its work, and the availability of the one extremely vital natural resource—water.

In approximate size, the Arsenal covers 6500 acres. Its activities are conducted in over 1500 buildings which are serviced by 85 miles of roads and 31 miles of railroad. Within its boundaries are two artificial lakes, three widely separated test-firing ranges, and two remote areas for the extremely hazardous activities.

As to the dollar-value of the Arsenal, its facilities are valued at over $500,000,000. The nature of these facilities varies, from the conventional to the nuclear. Conventional ammunition production lines, control laboratories and inspection systems are maintained in stand-by and are occasionally used in experimental or pilot-lot production. Nuclear weapons ammunition, components and devices are developed and produced in the necessarily special research laboratories, proof-testing facilities and production and pilot assembly lines.

History. Picatinny, or “water-by-the-hill”, was the name given by the Lenape Indians to the brook flowing under what is now called Picatinny Peak. Thus, two of the essentials for the manufacture of ammunition are implied by its name.

In the mid-eighteenth century a migrant blacksmith, Jonathan Osborne, was attracted by this plentiful water, by the supply of iron ore being mined over the mountain to the east, and by the inexhaustible forest of chestnut for his charcoal fires. At the foot of Picatinny Peak he built one of the first forges in New Jersey.

A few decades later this Middle Forge, as it was called, entered the ordnance picture. With the coming of the American Revolution, when the Continental Army fought its way across New Jersey, it was used to produce solid cannon
shot. At that time the plant had been taken over by a liberty-loving ironworker named Jacob Faesch, who had emigrated from Switzerland to help the hard-pressed Americans.

Early records fail to note the amount of ammunition produced. That it was considerable for that age may be inferred from the following known facts. To meet the demands, General Washington detailed 250 Hessian prisoners of war to augment the 440 workers assembled by Faesch from the scant local labor market. This working force of about 700 men turned out shot sufficient for waging a successful campaign; and for this, Faesch was made an American citizen by a special act of Congress.

Even in Revolutionary days, the valley was the scene of multiple ammunition activity. Faesch also manufactured fuses made of wood. As was specified for such components, his men moistened the powder “with a good grade of whisky” before tamping it into the fuse well.

Following the Revolution, the iron forge and powder mill in the Picatinny Valley shared the changes of fortune of the country’s industries. Except for brief periods of boom activity, particularly during the War of 1812 and the Civil War, they operated in comparative obscurity.

In 1879, Congress appropriated funds for the establishment of a powder depot near New York. Major F.H. Parker of the Ordnance Department inspected nine possible sites within 100 miles of Manhattan. On the basis of those attributes already mentioned, the Picatinny Valley site was chosen. On September 6, 1880, the War Department purchased 1866 acres in the valley for $62,750. The Secretary of War designated the reservation as the Dover Powder Depot.

Four days later he issued an order changing the name to the Picatinny Powder Depot. Six days later, on September 16, 1880, Major Parker was named the first Commanding Officer. In June 1883, the name was again changed to the U.S. Powder Depot.

For more than a decade, Picatinny (as variously named) was merely a storage and powder depot. The initial building, a magazine 200 by 50 feet, was built at a cost of $51,700. Four other magazines followed rapidly, as did officers’ quarters, stables for the horses and the necessary service buildings.

The first phase of the development of the Arsenal extended to the year 1902, and the history of the depot was one of gradual construction with the ultimate idea of an establishment for the storage of powder. However, a few years before the Spanish American War, the depot began assembling powder charges for cannon. This propellant charge loading, Picatinny’s first production activity, has never ceased.

In 1902, the need was felt for the storage of a war reserve of sodium nitrate, of armor-piercing projectiles and of high explosives. The second phase of Picatinny’s development began. Six projectile sheds and some nitrate buildings were erected. A year later, a temporary plant was installed for filling projectiles with Maximite and several thousand armor-piercing projectiles were filled with this explosive.

The third phase of the Arsenal’s development began with an appropriation in 1906 of $165,000 for the erection and equipage of a powder factory. This work was undertaken by Major B.W. Dunn, Jr., the inventor of Explosive “D”, which replaced Maximite for armor-piercing shell. In 1907, this, the Army’s first powder factory, was constructed. It was at this time also, and in line with its expanding activities, that the name was finally changed to Picatinny Arsenal.

Subsequent Commanding Officers supervised the powder factory and in the ensuing eight years, production increased from 3,000 to 9,000 pounds of cannon powder a day. Under the command of Major O.C. Horney, the Arsenal added other factories, including one for Explosive “D” and one for the manufacture of .30 caliber powder. In addition, an officers training school was established for instruction in the chemistry of explosives and interior ballistics.

At the outbreak of World War I, Picatinny was producing all sizes of propellants from .30 caliber up to 16-inch; for weapons from the rifle to the sea-coast gun. But possibly more important was the knowledge the Army obtained thru its development work. Quality was constantly improved and costs were constantly lowered. The investment in the training school was repaid many times in the preparation of the Ordnance officers to face difficult situations in action.

In the years following World War I, Picatinny started the melt-loading of projectiles on a production basis, and the development and manufacture of pyrotechnic signals and flares. This
latter research took pyrotechnics out of the "fireworks" class which had proved so ineffective during the war. It designed and produced an entirely different and effective group of pyrotechnics. In these years also, experimental plants were set up for the manufacture of more modern propellants, high explosives, fuzes and metal components. The manufacture of fuzes on a production scale was started.

The modern Picatinny Arsenal dates from July 10, 1926, the Saturday afternoon when lightning struck a tree overhanging a magazine at the neighboring Naval Powder Depot at Lake Denmark. The detonation of the depth bombs stored in that magazine, and minutes later, of two neighboring magazines, laid waste much of Picatinny. Since Saturday noon was, at that time, the end of the work-week, the loss of life was extremely limited for such a major disaster, with 18 fatalities (See Vol 6, E374-R to E377-R).

The Board of Officers investigating the disaster recommended not only the Arsenal's immediate reconstruction, but urged that more land and facilities be added, to the end that a bigger, better, and safer manufacturing and development Arsenal should result. The recommendation was followed. Within a few months, activities were resumed, the rubble was pushed back and the single-story brick magazines, which had survived the blasts, were reroofed and rewindowed. In these makeshift buildings the plans were drawn for the administration building and the laboratory group, which were the nucleus of the present facilities.

The subsequent story of Picatinny is revealed thru its accomplishments:

Long before World War II, the Axis powers were boosting their stockpiles of arms. By 1938, following the now infamous Munich Pact, President Roosevelt began to call for increased armament production in the U.S. When the Germans pushed the Allies into the sea at Dunkirk, Picatinny Arsenal was the only plant in the U.S. capable of producing large quantities of artillery ammunition and bombs, high explosives and pyrotechnics, fuzes and other essential ordnance.

It was no accident that Picatinny was ready. While the U.S. has no military ammunition industry in peace times, Congress always has permitted the Army certain funds for research and engineering work, which is the primary mission of Picatinny. As such, it always has been the Arsenal's function to be prepared to advise private industry on new and better ways to manufacture ordnance when the time comes. An all-important phase of this activity was the manufacture of munitions on a pilot plant basis.

The Ordnance Corps' sensitivity to the urgent demand for war material kept pace with the swift-moving events in Europe. Thus, most of the pilot plant operations at Picatinny were expanded to all-out assembly line production before Hitler overran the Low Countries.

At the time of the Japanese attack on Pearl Harbor, no other plant existed in the U.S. capable of making anything larger than small arms ammunition. There was no knowledge elsewhere; there were no detailed plans for whole industries elsewhere. Without the industrial "know-how" developed at Picatinny, the rapid conversion of commercial concerns to mass ammunition manufacture would have been impossible.

While waiting for private industry to convert its assembly lines for ammunition production, Picatinny filled the gap. Between July 1939 and September 1952, more than 7,500,000 bomb fuzes, almost 20,000,000 boosters, 44,000,000 artillery primers, 39,000,000 artillery fuzes, and countless millions of other items were turned out.

With the outbreak of war, Picatinny immediately set to the task of training workers. During the conflict, more than 8,000 men and women were trained in the highly specialized techniques peculiar to the mass production of all munitions other than small arms. In addition, almost 20,000 persons involved in munitions work visited Picatinny.

To illustrate the value of these efforts: in one year the job training methods, research projects and improved work developments originating at Picatinny, and passed along to outside plants, saved the Government more than $30,000,000. This accomplishment was recognized by Lt. Gen. Brehon Somervell, Chief of the Army Service Forces, and Maj Gen L.H. Campbell, Jr., Chief of Ordnance, in letters to the Commanding Officer.

Thus was proved the Army's foresight in maintaining Picatinny during the years of peace.
Only because of the Arsenal's ever awake research and development program was the United States able to turn to a ready source to meet the demands for information when the need arose.

To Picatinny's accomplishments in meeting the urgent needs for masses of ammunition and aid to industry must be added two others: the production of new types of ammunition to meet specific needs; and delivering them in time.

In 1944, the Navy needed 200 special bomb fuzes. Over one weekend the fuze parts were received from a firm in Milwaukee, the fuzes loaded and assembled, and delivered to a carrier-based plane from the Saratoga, then far out at sea in a task force on its way to Murmansk.

Still another illustration of Picatinny's problem-solving ability: Ammunition manufacturers had long depended exclusively on silk for cartridge cloth. Because of its high tensile strength and low ash content it made an ideal container for propellant load charge. America could not rely on silk as it did not control the supply. Cotton would be ideal from the standpoint of supply and low price, but was objectionable because of its high ash content and the danger of resulting embers in the gun barrel.

This was a problem to all the Allies: but it was a Picatinny researcher who solved it. Thru patient burning of samples of cotton cloth, for burning time and amount of residual ash, he narrowed down the fabrics to a few good possibilities. Then he traveled to cotton mills in New England and the South to seek still better cloth. Finally a cotton fabric was developed as a suitable substitute for silk.

The Ploesti oil fields were a vital source of petroleum for Hitler's forces. Special bombs were needed to blow up those fields. Picatinny Arsenal supplied these and the Ploesti installations vanished into thin air.

Other special bombs were needed to blow up dams on the Dnieper River in Russia and thus immobilize 600,000 Germans. The Arsenal planned the bombs, made them and shipped them. They did the job.

Still another illustration involves the English fog. American airmen there, in their around-the-clock bombing of German targets, suffered heavier casualties in landing on the fog-bound runways than during combat missions. A flare was needed which would develop 800,000 candle power, burn for at least five minutes, be able to penetrate mist and fog, develop little or no smoke, have a mount suitable for installation on new runways and be easy to ignite under the most adverse weather conditions. Picatinny's pyrotechnics engineers produced an even better flare; and the first 250 of them were flown to England, all within 60 days after the request was received.

During the Battle of the Bulge alone, these flares were credited with preventing more than 100 bombers from crashing.

Other problems of the airmen were solved at Picatinny. In 1943, the introduction of skip-bombing brought a special request. Because of the low altitude at which the bombing plane had to fly, a bomb with a delay fuze was required to permit the plane sufficient time to get away from the effective range of the explosion. In many instances, bombs were to be dropped from as low as 25 feet. Again, Picatinny came up with the answer: a fuze which would delay detonation of the bomb eight to eleven seconds.

Another instance of aid to the Air Corps involved its radio IFF System (Identification, Friend or Foe) to protect fighter and bomber planes against enemy attack from the rear when returning from a mission. More than 100 heavy bombers were grounded in the U.S. until Picatinny came thru with a vitally needed item. The situation was this: The IFF System was based on a combined radio transmitter-receiver in each plane, tuned to a secret wave length. When a plane came up behind the U.S. Aircraft, the pilot of the pursued plane knew immediately whether the one behind him was a friend or foe. As long as the enemy never put his hands on one of the transmitters-receivers, the secret would be safe. Air Corps Commanders knew, however, that sooner or later a U.S. plane would go down behind enemy lines and the secret would be no more. Picatinny was sent an "emergency" order to design, develop and produce a controlled explosive which, housed inside the trans-receiver, would blast the radio beyond restoration upon receiving any jar greater than that experienced in normal landing operations. The order was phoned from Washington and immediately the resources of the Arsenal were swung behind the assignment. The Technical
Division — operating behind sealed doors because the job was top secret — came up with the answer: a short, serrated metal tube containing just enough explosive to shatter the inside of the radio set without causing any damage to the plane. The development of this item was spiked with troubles. An essential part of the design was a plastic plug at one end of the tube. This required top precision machining of the mould for the plastic; when this was half ground, the two machinists were simultaneously drafted into the Army. In a rare adjustment to emergency, the discharge of the men was effected and 48 hours later they were back on the job. Without revealing the reason for the urgency, the grinders were pressured to speed up the job. It looked then as if they might complete it in less than six weeks instead of the estimated two months. Toward the end of the period the Arsenal received a demand: 150 “destroyers” within three days. This was on Sunday night. On Tuesday evening, 200 destructors were aboard a dispatch plane at Newark Airport.

These and hundreds of other difficult assignments were handled by Picatinny; and with similar dispatch. The civilian employment rose to 18,000, of whom 10,000 were women.

Buildings were expanded and new construction went on continuously. At a press visit to the Arsenal in 1941, Col W.E. Earned, Commanding Officer, told reporters: “We don’t need new buildings. We need ammunition. We can make it in tents, if necessary.” Unexpected realism was given this statement. Workers reporting to a new components building, not yet completed, found it weather-proofed with huge tarpaulins; but the miniature parachutes for flares rolled out on a 24-hour, three-shift basis.

In addition to producing ammunition, the Arsenal had to help get it to the front on time — and in good condition. Picatinny saw to it that the items were well packed. Packaging engineers were imported to supplement the Arsenal’s staff to develop better methods of packing bombs, explosives and ammunition. Engineers from private industry came to Picatinny to learn the science of packaging.

The close of this period of great war activity was marked by V-J Day. It also marked, faintly and hesitatingly at first, the beginnings of a new era — the establishment of Picatinny Arsenal as a modern research, development and engineering center. Gradually the installation converted its primary role to that of research and engineering of new ordnance to provide the Army with the most modern and effective means of combat.

The outbreak of hostilities in Korea belied the theory that the A-bomb would put an end to all wars, and it proved once more the importance of Picatinny’s role. When the North Koreans began using Russian-made T34 medium tanks in the middle of July 1950, the U.S. 8th Army’s toe-hold on Taejon began to slip. Even the reliable Bazooka, the rocket launcher that had stopped Rommel’s Tank Corps in Africa, could not stop the massive, heavier T34’s imported from Soviet Siberia. In the United States, a new and more powerful 3.5-inch Bazooka had just been perfected. At Picatinny, rocket shell for the improved weapon were produced on a pilot lot plant test basis. Immediately General MacArthur issued a dramatic call for the new Bazooka. If he was to be successful in fighting a delaying action until more troops arrived, he had to have the best ordnance available — if possible, better than the enemy’s. In less than 24 hours the test plant was expanded to full-scale assembly line production. As finished rockets came off the line, they were trucked to nearby Morristown Airport where waiting Army cargo planes loaded them for the trip to the other side of the world. Seven days after General MacArthur radioed his urgent demand for the heavier Bazookas, seven Red tanks were knocked out of the war. In a matter of a month the tanks no longer were a major menace.

When the hordes of bugle blowing North Koreans attacked U.S. positions, our troops found existing battlefield illumination unsatisfactory. To more effectively combat the enemy forces, they needed a pyrotechnic item which would illuminate the attackers from the rear, thus silhouetting them to make better targets for our riflemen. With typical GI ingenuity, they attached trip flares to tail fin assemblies which normally were used to launch conventional fragmentation grenades from rifle launchers. A make-shift arrangement, it was not the most efficient system. Picatinny’s pyrotechnics experts stepped into the picture. Within a matter of weeks, a new illuminating rifle grenade was developed and delivered to front line troops,
increasing the accuracy of our infantrymen during the nighttime raids.

Thus, during the Korean conflict, Picatinny reassumed its mission: meeting emergencies on time, and the mass production of the ordnance it had designed and developed.

In subsequent years, the Arsenal achieved one of its most notable achievements: the development of a nuclear shell which was capable of being fired from an artillery gun. This gave the United States its first nuclear artillery weapon, the 280mm Cannon. Picatinny’s success in producing the first nuclear shell inevitably led to the development of other sizes of atomic shell. To meet the need for a smaller, more mobile weapon than the 280mm, the Ordnance Corps in August 1952 called for an 8-inch nuclear shell capable of being used in both Army and Navy weapons. With the Korean Conflict still on and the future uncertain, a crash program was ordered. Though the 1953 armistice ended the fighting in Korea, work on the 8-inch shell continued to completion at a rapid pace. Besides, at that time, being the smallest package of nuclear ammunition achieved, the 8-inch shell was also notable because it was the first shell of any kind to use the lightweight, high strength metal, titanium.

Another application of nuclear energy to weaponry was in the nuclear demolition munition or “ADM”. These are pre-positioned nuclear warheads to which are linked firing devices that set off the explosion at the desired time. An ADM is easily transported and can provide as much blast effect as 500 railroad box cars of TNT. ADM’s may be emplaced above or below ground or underwater. The early ADM’s were simply nuclear bombs converted into time bombs. Later developments scaled down their size to the point where components of low-yield ADM’s could be man-carried to the emplacement site. The bulk and weight of larger yield ADM’s were also considerably reduced. One of Picatinny’s chief contributions to the ADM program was the development of a Universal Firing Device. This UFD, more compact and rugged than any of its predecessors, can convert any of the Army’s present or future nuclear warheads into a nuclear demolition munition.

A nuclear weapon created for infantrymen - the Davy Crockett - was developed under the technical direction of Picatinny. This weapon could be hand carried and fired from a tripod by two or three men. A heavier launcher with longer range was mounted on a jeep or armored personnel carrier and fired by two men. The lighter model was also vehicle-mounted. Great as was the destructive force of the Davy Crockett, its effective radius was kept small enough to protect the using forces as well as other friendly troops and civilian population from blast danger. The danger from radioactive fallout was thus minimized.

In the field of support devices, the Daisy photoflash cartridge was developed by Picatinny’s pyrotechnics experts. It was used in the optical tracking of intermediate and long-range missiles. Such tracking is for the purpose of evaluating the performance of the guidance and control mechanisms in missiles, thereby helping to improve the accuracy and reliability of these mechanisms. The tracking was achieved by affixing to the missiles a set of photoflash cartridges which fired at intervals while the missile was in flight and photographed by two or more bullistic cameras set at prefixed positions on earth. Since the firings were made at night, these cameras photographed not only the man-made star - the Daisy - but also the natural stars. With the positions of these natural stars as established reference points, the track of the Daisy was determined with great accuracy. This accuracy was greater than could be achieved by electronic means because it made tracking independent of any errors arising from the missile system itself and of distortions caused by the ionosphere. The Daisy cartridge weighed only two ounces but produced 20 million candlepower, visible at a distance of 1000 miles or more.

Another contribution of Picatinny’s pyrotechnics engineers was the development of the infrared decoy, used by planes to divert enemy missiles which are attracted to the plane’s infrared exhaust emanations. These decoys consist of high-efficiency infrared flares which are ejected by the plane at the appropriate time, attracting the missiles to the decoys and away from the plane.

Still another development of the pyrotechnic engineers was a nuclear timer, more accurate and rugged than any mechanical timer. Depending for its power on a nuclear battery, the
timer, in addition to its use in missile research, gave technicians the capability of pinpointing the location of nose cones thru sound tracking.

Among the missile systems to whose development Picatinny has contributed were the various members of the Nike family. The Nike-Ajax was the country’s first supersonic air defense guided missile fired from the ground to intercept and destroy enemy planes. The Nike-Hercules, capable of much longer ranges and higher altitudes, could carry a nuclear warhead. The Nike-Zeus was the first weapon designed to intercept inter-continental ballistic missiles. Picatinny designed the “business end” of these weapon systems, the warhead section, which includes the explosive payload plus its fusing, safing and arming devices. Ancillary handling and checkout equipment is also designed and developed by the Arsenal.

To defend against low-flying aircraft, Picatinny developed the warhead for the Hawk, which can be used not only to defend fixed installations but which can be carried by fast-moving combat troops in the field.

The Corporal, equipped with either a nuclear or conventional high-explosive warhead, gave the field commander a weapon with which he could hit tactical targets 75 miles away. Succeeding the Corporal came the Sergeant, which was air-transportable and could be quickly emplaced and fired by a relatively small crew under almost any weather or terrain conditions.

The Honest John, with the range of medium to long-range artillery, was designed to provide close-fired support in land combat operations. With a single round the Honest John could deliver as much demolition effect as several hundred artillery shells. The Lacrosse was another general support weapon that was not only powerful but was so accurate that it could be used to destroy small fortifications.

The Redstone was designed to deliver its nuclear or high explosive payload a distance of more than 150 miles. Its successor, the Pershing, is much smaller, lighter, and more mobile.

The Lance system enables the fielding of a nuclear capability with improved field readiness and greater versatility over the Sergeant, Honest John and Little John systems.

Although missiles and other nuclear items were the new weapons of the post-Korean period, the need for the older conventional gun-type weapons had not disappeared. Existing missiles were not as accurate or reliable as artillery guns and did not provide their rate of fire and responsiveness. For many uses, missiles were also much more expensive than gun artillery.

Picatinny Arsenal’s contributions to the recent military effort in Southeast Asia were substantial. The timely and quantitative production of bombs and other standard items of ammunition was accomplished until industry could regain its role. The Arsenal also responded to the need for the development of new and improved munitions during this period, including more effective fuses and safing and arming devices.

The development of a family of 40mm ammunition for helicopter and infantry was a typical example. Because of the broad spectrum of industrial facilities and processes which support the munitions program on a nationwide basis, a major effort at Picatinny in terms of manpower and technology effort is being expended to support a multi-billion dollar Plant Modernization Program for improvement of GOCO facilities to insure production operations that are modern, economical, safe, automated and non-polluting. A concomitant to the progress of Arsenal technology is an ever increasing awareness and application of the latest industrial pollution abatement technologies and a priority concern with environmental protection.

In the highly versatile 175mm gun, for which Picatinny developed the ammunition, the Army has a weapon superior to any World War II cannon. Picatinny also streamlined the 81mm and 4.2-inch mortar shell to provide greater accuracy and longer range. The lethality of the shell was considerably increased. Increased range was provided for the 105mm and 155mm howitzers.

Another weapon system which was developed and engineered for production by the Arsenal for Southeast Asia was Beehive ammunition of varying calibers which dispense great numbers of tiny, lethal steel darts. This type of ammunition proved effective in Southeast Asia since it lends itself to use against troops in frontal mass assault as well as those entrenched behind the cover of heavy jungle brush.

Historically, mines have been defensive wea-
pons. Their use has required time consuming operations to lay a field in expected avenues of enemy approach. In an effort to overcome this problem, the Arsenal conducted studies to determine the feasibility of rapidly emplacing mine fields from aircraft. During the height of the Southeast Asia conflict, such a system was designed, developed, produced in quantity and utilized in the field.

Advancing technology as well as this demonstration of potential utility of Mass Scatterable Mines led the Army to revise mine warfare doctrine and establish new requirements for a family of Scatterable Mines that could be rapidly and remotely emplaced by a variety of delivery systems. This requirement called for both Anti-Tank and Anti-Personnel Mine Systems. To this end, two first generation systems are well advanced in development. These are: the XM56, a helicopter delivered Anti-Tank Mine System, and the XM692, an artillery delivered Anti-Personnel Mine System. Other second generation systems which add increased versatility and capability are scheduled to follow.

Presently the Arsenal's scientists and engineers continue to explore ways and means of developing new and improved versions of existing munitions which would be required to meet the challenge of another time and a confrontation of a different nature. This it does thru its comprehensive and continuing program of research, in the nuclear as well as the non-nuclear field. Such efforts include missile warhead programs, aircraft weaponization, rocket assisted projectiles, tank weaponry, flare development, and similar projects, all of which are aimed at making the American soldier the world's best equipped fighting man.

Effective July 1973, the U.S. Army Armament Command was established as a Major Command of the U.S. Army Materiel Command, located at Rock Island, Illinois. Effective 30 September 1973, the U.S. Army Munitions Command and the U.S. Army Weapons Command were disestablished and merged into the operational command of this new Armament Command. Picatinny Arsenal, as a Commodity Center, presently reports organizationally to the U.S. Army Armament Command.

Refs: 1) N.F. Ramsey, ArOrdn 7, 1–8 (1926) (Historical background) 2) F.H. Miles, ibid, 9–12 (1926) (The Picatinny Arsenal Powder Factory) 3) G.C. Hale, ibid, 13–18 (1926) (Research activities at Picatinny Arsenal) 4) H.H. Zornig, ibid, 19–22 (1926) (Organization and administration of development work at Picatinny Arsenal) 5) J.P. Harris, ibid, 40–48 (1926) (Loading ammunition at Picatinny Arsenal) 6) C.J. Bain, ibid, 49–52 (1926) (High explosives at Picatinny Arsenal) 7) F. Olsen, ibid, 53–57 (1926) (The relation of Picatinny Arsenal to field service) 8) W.H. Tschappat, ibid, 131–34 (1926) (The Lake Denmark explosion; its effect on Picatinny Arsenal)

Picramates. Salts of Picramic Acid. See in Vol 1, A242-L to A243-L

Picramic Acid. See under 4,6-Dinitro-2-aminophenol in Vol 1, A241-R

iso-Picramic Acid. See under 2,6-Dinitro-4-aminophenol in Vol 1, A243-R

Pieramide. See under 2,4,6-Trinitroaniline in Vol 1, A409-R

PICRATES

The salts and additive compds of Picric Acid (PA) are usually included under picrates. For convenience, inorganic and organic picrates will be described separately.

PICRATES, INORGANIC

PA attacks all the commonly used metals except Al and Sn, with the formation of salts known as picrates. These salts can also be prepared by the action of PA on hydroxides or carbonates, or by other methods. Nearly all picrates are explosive, and are usually more sensitive than PA. Some picrates, eg, Pb Picrate, can serve as initiating agents. Many picrates detonate with such
violence that they can initiate an indefinite amt of PA; even wet PA can thus be expld (Ref 7)

The hazardous nature of the picrates is underscored in Urbalis's description of the construction of PA driers (Ref 11):

"The construction of picric acid driers presents certain difficulties because of the ready formation of picrates. Having this in mind, wood is mostly used as the construction material for driers, and any metal parts (screws, nails) should be made either of metals that form picrates with difficulty such as copper or aluminum, or of tinned metals or stainless steel. Floors should be made of wood covered with linoleum or concrete coated with asphalt. At the beginning of World War I when concrete floors were common in use, picric acid would with time form picrates with cationic constituents of the concrete: calcium, magnesium, sodium and iron. Washing the floor created conditions favourable for the penetration of picric acid into the concrete, and after several months a thick layer of picrates used to form. Any friction, as for example, by moving a bench around or any sort of blow, initiated an explosion of picrates all over the floor, causing fire or explosion in the drier. The inside walls should be plastered with plaster of Paris, since gypsum, being the salt of a strong acid, yields calcium picrate only with difficulty. Lining the walls of the drier section with white glazed wall-paper is recommended. Heaters for heating the drying air should not be placed inside the drying premises. Workman who have to enter the drying section should put on protective wooden-soled shoes with no nails in them. The floor should be swept frequently and washed with water."

Although metallic picrates have been known since as early as 1795 (Ref 4), there is still much confusion in regard to their compn and properties. The first application of picrates as expls seems to have been made in 1869 by Designolle of Fr, who proposed the use of K picrate, K nitrate and charcoal in various proportions. Fontaine proposed a mix of K picrate and K chlorate, while Brugere and Abel, independently, and about the same time (1869), proposed the use of mixts of Amm Picrate and K nitrate (Ref 7)

The first systematic study of metallic picrates seems to have been done in 1901 by Dupre

(Ref 2). This was followed by Will in 1906 (Ref 3), Silberrad and Phillips in 1908 (Ref 4), and Kast in 1911 (Ref 5). More recently (1938), Hopper of PicArsn (Ref 6) detd and described the expl properties of the following metallic picrates: Al, Cd, Cr, Cu, Fe^2+, Fe^3+, Na, Ni and Zn. In general, he prod the salts as cryst hydrates from aq solns by methods outlined by Silberrad & Phillips, and Kast. These were then dehydrated by heating at temps of 80 to 150°, depending on the ease with which the w of crystn could be driven off, to obtain the desired degree of hydration

The salts were identified by their metallic content, which was detd by standard lab methods. Their expln temps were detd by the method originated by H. Weber (Bull US Bureau of Standards 9, 119 (1913) and modified at PicArsn [PATR 1401 (1944)]. The sensitivity to impact was detd using the PicArsn app, described by H.S. Deck [ArmyOrdn 7, 34 (1926)], using a 2kg wt

According to Hopper, the relative sensitivity of metallic picrates depends largely upon the amts of w of crystn present. The highly hydrated forms are very insensitive, the lower hydrates are in general more sensitive, and the anhydrous forms most sensitive. The anhydrous salts, with the exception of Na, Amm, Al and Fe^3+, are more sensitive to impact than PA. Anhydrous Cu, Zn and Cd picrates are only slightly more sensitive, while anhydrous Ni picrate is especially sensitive, lying in the sensitivity range between MP and Tetryl

According to Thorpe's (Ref 7), the order of impact sensitivity of some of the metallic picrates is as follows; Pb > Fe > Co > Ni > Ba > Cu > Mn > Zn > Ca and Na, with Amm picrate being among the least sensitive

The sensitive anhydrous salts are obtained with difficulty by prolonged heating of the hydrated forms at temps above 100°

The picrates prep by Hopper, as well as other expl picrates, are described below

Refs: 1) Bell 6, 275–78, (134–45) & [262–65] 2) A. Dupre, MP 11, 92 (1901) 3) W. Will, SS 1, 209 (1906) 4) O. Silberrad & H.A. Phillips, JCS 93, 474–89 (1908) (Metallic picrates, with numerous refs, beginning in 1795) 5) H. Kast, SS 6, 8–9, 31–33 & 67–70 (1911) (Metallic picrates) 6) J.D. Hopper, JFrankInst
List of Inorganic Picrates

Most of the salts described below can be prepd by interaction of PA with the corresponding inorganic salt or base. As much as PA is only sparingly soln in w, it is advisable to dissolve the metallic salt (or base) in w, and then introduce the PA in a finely divided state. For example, the Ksalt (see below) can be prepd by saturating a hot K carbonate soln with powdered PA; \(2\text{Ca}_4\text{H}_2(\text{NO}_3)_2\text{OH}+\text{K}_2\text{CO}_3 \rightarrow 2\text{Ca}_4\text{H}_2(\text{NO}_3)_2\text{OK}+\text{H}_2\text{O}+\text{CO}_2\). When the liq is cooled, pale yellow acicular crystals separate out.

**Aluminum Picrate.** \([\text{C}_6\text{H}_2(\text{NO}_3)_2\text{O}]_3\text{Al}\); mw 711.81; N 17.73%; mp, fuses above 100° and explds on further heating. Can be prepd by the prolonged heating of one of its hydrates (such as di-, tetra-, deca-, or hexadecahydrate) to 100°. Its impact sensitivity is 16° vs 14° for TNT, as detd with the PicArsn app with a 2kg wt. The dihydrate, \([\text{C}_6\text{H}_2(\text{NO}_3)_2\text{O}]_3\text{Al}_2\text{H}_2\text{O}\), obtained by heating the decahydrate to 80°, is comparable in sensitivity to the anhydr salt, while the decahydrate is very insensitive. The expln temp is about 360°

Refs: 1) Beil 6, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS 93, 483 (1908) 3) J.D. Hopper, JFranklinInst 225, 224 (1938) 4) Davis (1943), 165

**Aluminum Picrate (Basic).** \([\text{C}_6\text{H}_2(\text{NO}_3)_2\text{O}]_2\cdot\text{AlO}_2\text{H}_2\text{O}\); mw 300.35, N 15.85%; reddish to pale yel needles which, when heated to 80°, change to the tetrahydrate, a pale yel powd which, on heating, decomp w/ expldg

Ref: Colver (1938), 331

**Ammonium Picrate (Explosive D, Dunnite, Ammonium trinitrophenolate).** \(\text{C}_6\text{H}_2(\text{NO}_3)_2\text{O}_3\cdot\text{NH}_4\)

- mp 246.14°; N 22.77%;
- OB to CO₂ -52%; exists in stable yellow and metastable red forms of orthorhombic crys; mp, decomp without melting >265°; d 1.717g/cc (it can be pressed to a d of 1.64g/cc at 100,000psi); RI at 20°;
- \(a_0\) 1.508, \(b_0\) 1.870 & \(c_0\) 1.907; \(Q_f\) 395cal/g;
- \(Q_w\) 800cal/g; \(Q_e\) 2745cal/g

**History.** Amm Picrate was first prepd in 1841 by Marchand, but it was not until 1869 that it was used by Brugère (see Vol 2, B318-R), in admixt with K nitrate, as a propint for the Chassepot rifle. Later, in 1888, it was patented by A. Nobel for use in Dynamites. It was adoptd as a mil expl by the US Army in 1901, and the US Navy in 1907. Its importance as an expl was based on its relative insensitivity to impact and friction, making it ideal for use in armor-piercing (AP) projectiles, even though it was slightly inferior to TNT in expl strength. For several years it was used mainly in conjunction with BlkPdr in projectiles. The usual loading consisted of Explosive D in the nose section with BlkPdr in the rear, however, from 1917 thru WWII, the Navy used it for AP common and high capacity projectiles of practically all calibers, as well as AP and common rocket warheads and AP aircraft bombs. The demand for Explosive D during WWII was quite high, increasing from 1,500,000lbs/month in 1942 to 6,500,000 lbs/month in 1944. During the last year of WWII, Composition A-3 (see Vol 3, C474-R) began to replace Explosive D in smaller anti-aircraft (AA) projectiles. However, the development of Jet-Assisted-Take-Off (JATO) units, which used a mixt contg 50% Explosive D, counterbalanced its replacement in AA missiles (Ref 11). Currently, Explosive D is no longer used as a bursting-charge expl in shells, having been displaced by more modern expls of greater strength

**General Properties.** Chemically, Explosive D is not very reactive. It is decompd into PA and ammonia by strong alkalis. At 0°, it absorbs one molecule of ammonia, but loses this at 26°. When maintained at its mp, it decomp

As stated above, Explosive D is remarkable chiefly for its insensitivity to shock, which
permits its use in AP projectiles. It has a relatively low expln temp test value, and is slightly sensitive to frictional impact as indicated by friction pendulum and rifle bullet impact test results (see below). It is relatively insensitive to initiation, as it cannot be detonated completely in the sand test by Pb Azide or MF alone, but it can be detonated by DDNP. When stored at 50° for two years, Explosive D is sensitized so that it can be detonated with MF alone. Subsequent storage at ordinary temp restores its previous insensitivity.

Explosive D is approx 80% as brisant as TNT, as indicated by sand tests, but fragmentation tests in shell have shown it to be about 95% as brisant. Both expls have about the same rate of detonation at a d of 1.56g/cc; hence, approx equality of brisance would be expected. The rate of detonation of Explosive D has been found to be somewhat affected, particularly at lower loading densities, by the granulation of the material, but this effect is not pronounced. Its expl strength is 98% that of TNT, as evidenced by the ballistic pendulum test (see below).

As judged by vacuum stability test data (see below), Explosive D is of a very high order of stability. The material has been found to withstand storage at ordinary temps for a period of twenty years with no evidence of deterioration, and at 50° for more than five years without marked deterioration.

Explosive D should not be exposed to moisture, since w reduces its strength and sensitivity to detonation. Moisture also increases its reactivity with metals such as Pb, K, Cu, Fe, etc, to form extremely sensitive comps. This reactivity requires that all projectiles loaded with this material must have contact areas covered with acid-proof paint.

When Explosive D is ignited in an unconfined state, it burns slowly, emitting dense black smoke without detonation. When confined and heated to its ignitn temp, it will expid. When detonated completely, it emits a dense cloud of black smoke with a sooty deposit and an odor of ammonia. When an incomplete detonation is obtained, a yel smoke is observed, together with unburned particles of Explosive D.

Explosive D which has been pressed into and removed from projectiles or other ammo is much more sensitive to shock than new or unused material. Therefore, reclaimed material should not be pressed or loaded into ammo items until it has been recrystd (Ref 12).

The destruction of Explosive D can be accomplished by chem decompn by dissolving the expl in thirty times its wt of a soln made from one p of Na sulfide in six p of w (Ref 13).

**Preparation.** Explosive D is manufd by suspending PA in hot w and neutralizing it with gaseous or liq ammonia. As the picrate is formed, it goes into soln; on cooling, it pptts out. An excess of ammonia leads to formation of the red form of Amm Picrate, and should be avoided. The separated crsytls are washed with cold w to remove any excess ammonia, and dried.

**Solubility.** In gms/100gms of solvent:

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>–</td>
<td>0.70</td>
<td>1.02</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>75</td>
</tr>
<tr>
<td>Alcohol</td>
<td>0.51</td>
<td>0.69</td>
<td>–</td>
<td>1.05</td>
<td>1.89</td>
<td>3.62</td>
<td>–</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>0.29</td>
<td>0.30</td>
<td>–</td>
<td>0.38</td>
<td>0.45</td>
<td>0.56</td>
<td>–</td>
</tr>
</tbody>
</table>

**Brisance.** Sand Test, 200g bomb: 37.5 to 39.5 g sand crushed vs 48.0g for TNT (78 to 82.5% TNT). Plate Dent Test: Method A for pressed confined charge, 91% of TNT at d 1.50g/cc.

**Explosion Temperature.**

<table>
<thead>
<tr>
<th>Seconds</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 (no cap used)</td>
<td>405</td>
</tr>
<tr>
<td>1</td>
<td>367</td>
</tr>
<tr>
<td>5</td>
<td>318 (decomps)</td>
</tr>
<tr>
<td>10</td>
<td>314</td>
</tr>
<tr>
<td>15</td>
<td>299</td>
</tr>
<tr>
<td>20</td>
<td>295</td>
</tr>
</tbody>
</table>

**Friction Pendulum Test.** Steel shoe, unaffected.

**Heat of Combustion.** 685kcal/mole at Cv (Ref 1, [262]); 2890cal/g at Cv (Ref 1 [134]); 2745cal/g at Cp

**Heat of Explosion.** 800cal/g

**Heat of Formation.** 395cal/g or 97.04kcal/mole

**Hygroscopicity.** At 100% RH and 25°, gains 0.1% to equil

**Impact Sensitivity.** PicArsn app, 2kg wt, 16-17" vs 12-14" for TNT

**Initiation Sensitivity.** Min charge of MF to initiate 0.4g of Explosive D loaded at 200am/sq inch in detonator cap is 0.85g vs 0.26g MF necessary to initiate 0.4g TNT.
Loading Density.

<table>
<thead>
<tr>
<th>d, g/cc</th>
<th>psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>3,000</td>
</tr>
<tr>
<td>1.41</td>
<td>5,000</td>
</tr>
<tr>
<td>1.47</td>
<td>10,000</td>
</tr>
<tr>
<td>1.49</td>
<td>12,000</td>
</tr>
<tr>
<td>1.51</td>
<td>15,000</td>
</tr>
<tr>
<td>1.53</td>
<td>20,000</td>
</tr>
<tr>
<td>1.64</td>
<td>100,000</td>
</tr>
</tbody>
</table>

**Power.** Ballistic Mortar, 99% TNT

**Pressure.** Max theoretical; when expld adiabatically at C_v, 8956kg/cm² at d 1.5g/cc and 9553 kg/cm² at 1.6g/cc. These are 113% of the corresponding values for TNT

**Rifle Bullet Sensitivity.** 10 trials, 7 unaffected, 3 partly burned

**Sensitivity to Electrostatic Discharge.** Thru 100 mesh material, confined 6.0 joules, unconfined 0.025 joules (Ref 10)

**Stability.** Vacuum Stability Test, 5g sample:

<table>
<thead>
<tr>
<th>°C</th>
<th>gas/40 hrs</th>
<th>0.2</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>120</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

100° Heat Test: % loss 1st 48 hrs, 0.1; % loss 2nd 48 hrs, 0.1; expln in 100 hrs, none

130° Heat Test: No expln and not acid in 300 min

**Toxicity.** Explosive D is not markedly toxic, but it discolors the skin and may cause a dermatitis in some cases. Inhalation of the dust should be minimized, and frequent baths and changes of clothes are desirable for those working with the material in quantity (Ref 14)

**Velocity of Detonation.** 4750m/sec at d 1.0g/cc, and 7040m/sec at d 1.60g/cc with a 2.5x40cm unconfined charge; 6850m/sec at d 1.55g/cc for a 1.0 inch charge diameter. It can be calculated approx from the formula, V=960+3800d, where d is density in g/cc, and charge diameter of 1.0 inch is employed

The requirements of the US Armed Forces are described in Military Specification MIL-A-166C (6 January 1975) entitled, “Ammonium Picrate (Explosive D)”. It covers one grade of material, representing two classes with respect to granulation. Class 1 material (coarse) is intended for use in the press-loading of shells, while Class 2 (fine) is used for the manuf of Picratol and other compns. The requirements are as follows:

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface moisture and volatile content, %, maximum (max)</td>
<td>0.10 —</td>
</tr>
<tr>
<td>Total moisture content, % max</td>
<td>0.20</td>
</tr>
<tr>
<td>Ammonium picrate purity, % min</td>
<td>99.0 99.0</td>
</tr>
<tr>
<td>Sulfates (as sulfuric acid), %, max</td>
<td>0.10 0.10</td>
</tr>
<tr>
<td>Chloroform soluble impurities, % max</td>
<td>0.10</td>
</tr>
<tr>
<td>Water insoluble material, % max</td>
<td>0.10 0.10</td>
</tr>
<tr>
<td>Irritant contaminants (as chlorine) parts of chlorine per million, max</td>
<td>50 ** —</td>
</tr>
<tr>
<td>Ash, %, max</td>
<td>0.1 0.1</td>
</tr>
<tr>
<td>Acidity and alkalinity (as picric acid or ammonia), % max</td>
<td>0.025 0.025</td>
</tr>
</tbody>
</table>

Color

Yel to Yel to

Om Om

* The picric acid used to make Class 2 ammonium picrate shall be by the nitration of phenol and shall contain no material salvaged from trimmings or from loading operations.

** Not applicable to ammonium picrate made from picric acid produced by the nitration of phenol

The color requirement is intended to cover the unavoidable presence of a small amount of the red form of Explosive D in admixed with the yel form. The requirement with respect to irritant contaminants represents a control of the purity of PA used in manuf when this is made by the dinitrochlorobenzene process. The chloroform soluble impurities requirement also represents a control of the nature of impurities present in PA manufd by a process other than the nitration of phenol.

The granulation of the applicable class of Amm Picrate shall be as specified in Table 2...
### Table 2: Granulation Requirements for Ammonium Picrate

<table>
<thead>
<tr>
<th>US Standard Sieve No</th>
<th>Percent by Weight Class 1</th>
<th>Percent by Weight Class 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thru No 12, min</td>
<td>99.9</td>
<td>-</td>
</tr>
<tr>
<td>Thru No 40, min</td>
<td>-</td>
<td>99.5</td>
</tr>
<tr>
<td>Retained on No 70, min</td>
<td>60.0</td>
<td>-</td>
</tr>
<tr>
<td>Retained on No 70, max</td>
<td>-</td>
<td>20.0</td>
</tr>
<tr>
<td>Thru No 200, max</td>
<td>5.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Bulk density (applicable to Class I only). The bulk density of the Amm Picrate shall be 0.82 g/cc min. In order to comply with this requirement on recryst Amm Picrate, the manufacturer shall be allowed, if necessary, to recryst all such material solely from w, and, in addition, may use as many w washes as required for the resulting material to pass the requirement


Barium Picrate. \([\text{Ba}_2(\text{CH}_3\text{CO}_2)_2] \cdot (\text{C}_6\text{H}_6\text{O}_7\text{N}_3)_2\), with 4H_2O or 7H_2O; yel crysts, expld on heating

Reffs: 1) Beil 6, [264] 2) R. Weinland & A. Hendricksen, Ber 56, 529, 533-4 (1923)

Barium-Picrate-Acetate. \((\text{Ba}_2(\text{CH}_3\text{CO}_2)_2) \cdot (\text{C}_6\text{H}_6\text{O}_7\text{N}_3)_2\), with 4H_2O or 7H_2O; yel crysts, expld on heating

Reffs: 1) Beil 6, [264] 2) R. Weinland & A. Hendricksen, Ber 56, 529, 533-4 (1923)

Cadmium Picrate. \((\text{Cd}_2(\text{NO}_2)_3\text{O})_2\) Cd, mw 569.70, N 14.76%, yel powd which exects violently at 336-41°. Was obtained by heating one of its hydrates at 80-150°. Silberrad and Phillips (Ref 2) reported on the hepta- and pentahydrates, while Hopper (Ref 3) reported on the octahydrate. Sensitivity of the anhydr salt is 12° vs 14° for TNT, as dted with the PicArsn app using a 2kg wt. The value for the octahydrate is 35°, making it less sensitive than BlkPdr dust

Reffs: 1) Beil 6, 277 & [264] 2) O. Silberrad & H.A. Phillips, JCS 93, 482 (1908) 3) J.D. Hopper, JFrankInst 226, 223 (1938)

Calcium Picrate. \((\text{Ca}_2(\text{NO}_2)_3\text{O})_2\) Ca, mw 497.38, N 16.90%, yel powd which exects violently at 323-28°. It is obtained when the decahydrate is heated to 80°

Reffs: 1) Beil 6, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS 93, 479 (1908)

Cerium Picrate. \((\text{Ce}_2(\text{NO}_2)_3\text{O})_2\) Ce, mw 824.45, N 15.29%, brown powder which exects violently at 306-13°. Can be prep by heating either its trihydrate or undecahydrate

Reffs: 1) Beil 6, 277 2) O. Silberrad & H.A. Phillips, JCS 93, 485 (1908)
Cesium Picrate. $\text{Cs}_2\text{H}_2(\text{NO}_2)_3\text{O}_4\text{Cs}$, mw 361.01, N 11.64%, yel needles; explnds with moderate violence at 277–87°. It has been used to surface seed RDX charges used in exprn driven magneto-hydrodynamic generators (Ref 3)


Chromium Picrate. $\text{C}_3\text{H}_6\text{O}_{16}\text{N}_4\text{Cr}_2\text{H}_7\text{O}_2$, mw 1695.09, N 12.04%. Green crysts of this basic salt were prepd by Silberrad and Phillips (Ref 2) by mixing equiv quantities of Ba picrate and Cr sulfate, and evap the filtrate in vacuo over sulfuric acid. It yields an anhydr salt when heated to 150°. Hopper (Refs 3 & 4) claimed to have prepd the salts with 13H$_2$O and 1H$_2$O; both expld at about 330°. The impact sensitivity of the 13H$_2$O salt (PicArsn app with 2kg wt) was 36° vs 8° for the 1H$_2$O salt (TNT=14°)

Note: The violet form of Cr sulfate was used in the double decompn reaction with Ba picrate, since the sulfate ion of the green form was not completely ppt by Ba comods

Refs: 1) Beil 6, 278 2) O. Silberrad & H.A. Phillips, JCS 93, 486 (1908) 3) J.D. Hopper, PATR 764 (1936) 4) Ibid JFrankInst 225, 224 (1938) 5) Davis (1943), 165

Cobalt Picrate. $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{Co}$, mw 371.03, N 22.66%, brown powder which expls with moderate violence at 320–25°. Can be obtained by heating any of its hydrates to 150°

Refs: 1) Beil 6, 278 & [264] 2) O. Silberrad & H.A. Phillips, JCS 93, 487 (1908)

Copper Picrate (Cupric Picrate). $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{Cu}$, mw 520.85, N 16.14%, greenish-yel powder, very hygroscopic. Explnds violently at 282–87° (Ref 2) and 373° (Ref 3).

Can be prepd by heating any of its hydrates to 80–150°. Its impact sensitivity is 12° vs 14° for TNT, using the PicArsn app with a 2kg wt (Ref 4). Hopper claimed to have prepd the tri-

hydrate, which expld at 300°; its impact sensitivity was 19° (Ref 4)


Ferric Picrate. $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_3\text{Fe}_{11}\text{H}_2\text{O}$, mw 938.4, N 13.44%, yellowish-red needles. Was prepd in 1911 by Kast by treating a hot satd soln of ferric sulfate with Ba picrate (Ref 1). Hopper (Ref 2) prepd several hydrated ferric picrates of unknown w content which expld at 295°. Their impact sensitivity ranged from 6° (for material dried at 150°), to 36° (for material dried at 25°) (PicArsn app with 2kg wt)

Refs: 1) Beil 6, (135) 2) J.D. Hopper, JFrankInst 225, 224 (1938)

Ferrous Picrate. $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{Fe}$, mw 513.15, N 16.38%, dark green powder which expld feebly at 315–20°. It was obtained by drying the octahydrate in a vac dessicator over sulfuric acid. Its impact sensitivity was 14–15° (vs 14° for TNT). The octahydrate was obtained by treating a hot concd aq soln of ferrous sulfate with Ba picrate; yel hexagonal prisms which turned brown on standing; impact sensitivity 36°

Note: According to Thrope (Ref 3), the anhydr ferrous salt is very sensitive; in 1901, it caused a fire at Huddersfield

Refs: 1) Beil 6, (135) 2) O. Silberrad & H.A. Phillips, JCS 93, 487 (1908) 3) Thrope 4, 482 (1949)

Lead Picrate. $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{Pb}$, mw 663.41; N 12.67%; yel crysts; mp, expls violently at 270–81°. Can be obtained by heating either the monohydrate or tetrahydrate to 150°. The tetrahydrate is obtained in the form of silky yel needles when an aq soln of PA is treated with Pb carbonate. The Ger method of prepn is given under Bleipikrat in Ref 9

The impact sensitivity of the anhydr salt is, according to Taylor and Rinkenbach, 4cm when using a 500g wt. This means that it is more
sensitive than MF (24cm). When detd on the Pic-Arsn app using a 2kg wt, its sensitivity was 2" vs 14" for TNT. Its friction sensitivity, as detd by the Friction Pendulum Test, was also high (Ref 3)

Pb picrate monohydrate was patented in Fr in 1872 for use in caps and primers (Ref 4). It was used in Ger (Refs 5 & 6) for the prep of ignition mixts in "fusehead" muntn. Belcher (Ref 10) reported that during the usual qm inorganic analytical procedure, samples contg the Pb and salicylate radicals can lead to the formation and possible detonation of Pb picrate.

This arises during evapn of the filtrate with nitric acid, after pptn of the Cu-Sn group metals with hydrogen sulfide. Salicylic acid is converted under these conditions to PA, which in presence of Pb, gives exp Pb picrate. An alternative scheme is described which avoids this possibility


Note: Several expl basic Pb picrates are listed in Bell, such as:
1) 2Pb(C₆H₅O₂N₃)₂+3PbO+8H₂O; pale yel, microscopic crsps which expld violently ca 180°; 2) Pb(C₆H₅O₂N₃)₂+4PbO; dark yel, microscopic plates; explds on impact or when brought in contact with a flame. It was prepd by A.G. Lignose (Refs 1 & 3) from 2 moles of PA and 5 moles of Pb oxide in hot w. It is insol in hot w. Friedericke (Ref 2) prepd the basic salt by adding an alkaline soln of PA dropwise to a soln of a Pb salt while the latter was agitated. He proposed its use in primers, percussion caps and detonators

Refs: 1) Bell 6, 278 & [264] 2) W. Friedericke, BritP 192830 (1923) & CA 17, 3255 (1923) 3) A.G. Lignose, GerP 407416 (1925); Ibid, ChemZtr 1925, 1, 2484

Lead Methoxy Picrate. C₇H₇N₃O₅Pb, mw 482.35, N 8.71%; dark yel polycryst solid; mp, when heated it decomps with a loud crack; on slow decomn in a DSC app, the thermogram displayed a small endotherm at 207° and a prominent exotherm at 247° which marked its decomn; impact sensitivity, 4" (10% value, Pic-Arsn app, 2kg wt); exposn temp (5 sec value), 264°; brittleness (crushed sand), 28.6g; Q₆ 1555.9cal/g; Q₆ 405.4cal/g; insol in w, sol in dimethyl sulf oxide and dimethyl formamide

Prepd by treating methoxy picric acid with Pb hydroxide. It loses its OCH₃ group thru hydrolysis to form normal Pb Stypnate. The OPbOH group displays acidic behavior in soln. The expl properties of Pb methoxy picrate are similar to those of n-Pb Stypnate


Lithium Picrate. C₆H₂(NO₂)₂O.Li; mw 235.05; N 17.88%; pale yel powder which rapidly re-absorbs one mole of H₂O; mp, explds with moderate violence at 318—23°, d 1.724—1.740 g/cc at 20°. Can be prepd by heating its hydrates

Refs: 1) Bell 6, 276 & [263] 2) O. Silberrad & H.A. Phillips, JCS 93, 474 (1908)

Magnesium Picrate. [C₆H₄(NO₂)₂O]₂Mg; mw 481.60, N 17.45%; explds feebly at 367—72°. Can be prepd by heating one of its hydrates to 150°

Refs: 1) Bell 6, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS 93, 474 (1908)

Manganese Picrate. [C₆H₄(NO₂)₂O]₂Mn, mw 512.23; N 16.41%; yel powder, explds violently at 325—30°. Can be obtained by heating any of its hydrates to 150°

Refs: 1) Bell 6, 278 2) O. Silberrad & H.A. Phillips, JCS 93, 486 (1908)
Nickel Picrate. \([\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2\text{Ni}\); mw 516.01; N 16.29%; green powder, expls at 335–40°. Can be prepd by heating one of its hydrates. Hopper (Ref 3) gives the expln temp for the hexahydrate as 390°, and the impact sensitivity for the anhyd salt as 4” vs 14” for TNT using the PicArsn app with a 2kg wt

Refs: 1) Beil 6, 278 2) O. Silberrad & H.A. Phillips, JCS 93, 488 (1908) 3) J.D. Hopper, JFrankInst 226, 223 (1938)

Platinum Base Picrates. Some compds cntg Pt and PA are expl, for example:

- \([\text{Pt}(\text{CH}_3\cdot\text{S.CH}_3)_4]\) \([\text{C}_6\text{H}_2\text{O}_2\text{N}_3]_2\); N 9.32%; yel scales; expls on heating;
- \([\text{Pt}(\text{C}_2\text{H}_5\cdot\text{S.CH}_2\cdot\text{CH}_2\cdot\text{S.C}_2\text{H}_5)_2]\) \([\text{C}_6\text{H}_2\text{O}_2\text{N}_3]_2\); N 8.8%; yel solid; expls on heating

Refs: 1) Beil 6, (135) 2) L. Tschugaeff & W. Chlopin, ZAnorgChem 86, 251, 253 (1914)

Potassium Picrate. \(\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OK}\); mw 267.20; N 15.73%; reddish yel or green rhombic crystals; mp, expls with moderate violence at 310–166°; d 1.852 at 20°. It was first prepd in an impure state in the 17th century by J.R. Glauber (1603–1668) by dissolving wood in nitric acid, and neutralizing the resulting mixt with potash.

K picrate is prepd by neutralizing a hot aq soln of K carbonate with a hot PA soln, and filtering off the crystals that separate when the soln cools. It is sol in w to the extent of 0.5g/100g at 15°, and 2g/100g at 100°; in alc, 0.2g/100g at 25°. Ql is 621.8kcal/mole; impact test, 2°; expl temp test value, 370°. K picrate is of the same order of stability as Explosive D, but it is less brisant. When subjected to contact with a flame, it deflagsrates with a loud report (Ref 6). Mixts of K picrate with oxidizing agents, such as K nitrate, only burn when ignited, but are sensitive to shock (Ref 7).

According to Sarrau & Vieille (Ref 4), K picrate of d 0.5g/cc decomp on expln as follows:

- \(16\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OK} \rightarrow 4\text{KCN}+6\text{K}_2\text{CO}_3+21\text{CO}_2+52\text{CO}_2+2\text{N}_2+6\text{CH}_4+4\text{H}_2\) 7°C

Based on this equation, its "caractéristique théoriques" values were: \(q_0\) (vol of gas at 0° and 760mm), 549/kg; \(f\) (force specific), 6352; \(t\) (temp of expln), 2779°; \(\alpha\) (sovolume), 0.658; \(P\) (action explosive), 332 T.m.

K picrate was used as early as 1869 in expls, such as pouder Designolles (K picrate + K nitrate + charcoal) and pouder Fontaine (K picrate + K chlorate). It has also been used in pyrotechnic whistle compns (Ref 8), proplnts such as Ballistite, and in some primer mixts, ie, K picrate, Pb picrate & K chlorate (Ref 4).

Refs: 1) Beil 6, 276, (134) & [263] 2) E. Sarrau & P. Vieille, MP 2, 151 (1884) 3) O. Silberrad & H.A. Phillips, JCS 93, 476 (1908)

Vennin, Burlot & Lécorché (1932), 453
5) T. Tucholski, RocznikiChem 18, 840–9 (in Ger 849–50) (1938) & CA 33, 6691–2 (1939)

(Reduction decomp of K picrate) 6) Davis (1943), 63, 72, 293 & 417
8) Ellern (1968), 183

Rubidium Picrate. \(\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{ORb}\); mw 313.58; N 13.40%; yel needles which expld with moderate violence at 300–15°; also expld on impact

Refs: 1) Beil 6, 276 & [263] 2) O. Silberrad & H.A. Phillips, JCS 93, 476 (1908)

Silver Picrate (also called Pikratol in Ger). \(\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OA\text{g}}\); mw 335.98; N 12.51%; fine yel needles; mp, 315° with decomp; bp, expld ca 335°, or when brought in contact with an open flame; was not ignited or detonated by the spark of a fuse when compressed in a detonator cap. Can be prepd by dissolving Ag oxide in a hot satd PA soln (Ref 3)

Ag picrate was prepd in 1809 by Chevreul, and recognized by Liebig in 1888 as an expl.

Silberrad and Phillips (Ref 2) established its formula, and stated that it expld freely at 336–44°. Solubility in 100g of solvent at 25°: \(\text{H}_2\text{O}, 1.61; \text{eth}, 0.019; \text{acet}, 3.117; \text{& 95% alc}, 0.978g\)

According to Taylor & Rinkenbach (Ref 4), the sensitivity to impact with a 500g wt is 34cm vs 24cm for MP and 43cm for L.A. It is fairly insensitive to friction, as detd by the Friction Pendulum app

Silver Ammonia Picrate. [Ag(NH₃)₂]⁻
[C₆H₅(NO₂)₃]Cl, mw 682.23; N 28.75%; yel crystals; explos violently when heated above its mp
Refs: 1) Beil 6, [263] 2) E. Ephraim, Ber 54, 404 (1921)

Sodium Picrate. C₆H₅(NO₂)₃ONa; mw 251.10; N 16.74%; yellowish needles, which explos on being heated to 310–150°C (Ref 2). Sol in w and alc. Can be prep'd by heating its monohydrate to 150°C; which in turn can be prep'd by the action of Na carbonate on an aq soln of PA

According to Hopper (Ref 3), the monohydrate explos at 360°C, and its impact sensitivity is 17" vs 15" for anhyd Na picrate, vs 14" for TNT (PicArtn app with a 2kg wt)

Na picrate deflagrates on flame contact, and retains this property when mixed with other materials. It has been used in expl and pyrot comps in lieu of K picrate (Ref 5)

Note: Sodium Picrate, Double Salts of. When an aq soln of Na picrate (3 moles) is stirred and heated with 3 moles of finely powdered Ba or Pb picrate, the resulting double salts are less sensitive to impact than the single salts (and for this reason are less dangerous to handle). The same can be said for other picrate double salts (Ref 4)


Strontium Picrate. [C₆H₅(NO₂)₃.]₂Sr, mw 544.92; N 15.43%; yellow salt; explos fairly violently at 340–45°C. Can be prep'd by heating any of its hydrates to 200°C. The monohydrate is a yel powd which explos at the same temp as the anhyd salt

Refs: 1) Beil 6, 277 2) O. Silberrad & H.A. Phillips, JCS 93, 479–80 (1908)

Thallium Picrate. C₆H₅(NO₂)₃OTl; mw 432.48; N 9.72%; yel needles; mp, explos feebly at 273–75°C. Can be prep'd by dissolving Tl carbonate in aq PA, and partially evap the filtrate. Expols on heating or by impact

Refs: 1) Beil 6, 277 & (135) 2) O. Silberrad & H.A. Phillips, JCS 93, 484 (1908)

Thorium Picrate. Th(C₆H₅O;N₃)₄.10H₂O, mw 1324.68; N 12.69%; yel needles; mp 52–53°C; explos on contact with a flame

Refs: 1) Beil 6, (135) 2) G. Karl, Ber 43, 2068 (1910)

Zinc Picrate. [C₆H₅(NO₂)₃]₂Zn; mw 522.67; N 16.08%; brownish-yel powd; mp, explos violently at 350–55°C. Can be prep'd by heating one of its hydrates to 150°C. According to Colver (Ref 3), its impact sensitivity, as detd with a 2kg wt, is 60cm, which is comparable to that of PA

Refs: 1) Beil 6, 277, (135) & [264] 2) O. Silberrad & H.A. Phillips, JCS 93, 481 (1908) 3) Colver (1938), 334

Zirconium Picrate. [C₆H₅(NO₂)₃]₄Zr; mw 1003.66; N 16.75%; yel needles; mp, explos at 317–22°C. Can be prep'd by adding Zr carbonate to aq PA

Refs: 1) Beil 6, 278 & [264] 2) O. Silberrad & H.A. Phillips, JCS 93, 484 (1908)

PIRCRRATES, ORGANIC

These compds can be prep'd, in general, by dissolving the respective organic compds (hydrocarbons, nitrohydrocarbons, amines, phenols, etc.) in warm alc solns of PA, boiling the mixt., and then cooling it to crys out the resulting picrate

Organic picrates are usually more stable than PA, less sensitive to shock or heat and less corrosive to metals

Some organic picrates of nitrocompds are described in Beilstein under these compds, and this system is followed herein. Following is a
selected list of compds, taken primarily from the section on PA in Beilstein, which are more or less expl. The expln temps of many of the listed organic picrates were detd by R.J. Datta and N.R. Chatterjee, JCS 115, 1007–8 (1919):  
**Acenaphthene Picrate.** C_{14}H_{10}^+ + C_6H_5O_7^-N_3; orange-red prisms; mp 161–62°; expls at 412° (Beil 6, 273, (132) & [260])  
**Allylamine Picrate.** C_3H_7N^+ + C_6H_5O_7^-N_3; lemon yel needles; mp 140–41°; expls at 270°  (Beil 6, 283)  
**Aniline Picrate.** C_6H_4(NO_2)_2OH + C_6H_5NH_2^-; yel crysts; mp, decomps at 165°, expls at 398°  (Beil 12, 120 & [143])  
**Atropine Picrate.** Plates; mp 173–75°; expls at about 460°  (Beil 21, 30)  
**Azidoguanidine Picrate.** N_3C(NH)NH_2.HOC_6H_4(NO_2)_2; expls on heating but not on impact  [CanNatResCouncil Rept (Feb 17, 1942)]  
**Cinchonidine Picrate.** Expls at about 260°  (R.J. Datta & N.R. Chatterjee, JCS 115, 1008 (1919)); 2C_5H_9NO_3 + 3C_6H_5O_7^-N_3; yel crysts; mp 194–95°; expls at about 268°  (Beil 23, 430)  
**Guandine Picrate.** CH_3N_3^+ + C_6H_5O_7^-N_3; yel crysts; expls at about 498°  (Beil 6, 279 & [265])  
**Hexamethylenetetramine Picrate.** C_6H_12N_4^+ + C_6H_5O_7^-N_3; yel needles; mp, expls at about 360°  (Beil 6, 586)  
**Hydrazine Picrate.** N_2H_4^+ + C_6H_5O_7^-N_3; yel needles from alc; mp, 201.3° (184°), expls at about 385°  (R.J. Datta & N.R. Chatterjee, JCS 115, 1007 (1919) & Beil 6, 276 & [263])  
**Indene Picrate.** C_9H_8^+ + C_6H_5O_7^-N_3; golden yel needles; mp 98°; very expli in the dry state; decomps slowly in air  (Beil 6, 271 & [259])  
**d-Lysine Picrate.** C_6H_14O_2N_2^+ + C_6H_5O_7^-N_3; crysts; mp, expls on slow heating  (Beil 6, 287 & [139])  
**Naphthalene Picrate.** C_10H_8^+ + C_6H_5(NO_2)_2OH; golden yel needles; forms eutectic mixts with PA; mp 149–151.5°; expls at 484°  (Beil 6, 272, (132) & [259])  
**a-Naphthol Picrate.** C_10H_8O + C_6H_5O_7^-N_3; yel orange needles; mp 189–90°; expls at about 458°  (Beil 6, 605 & [306])  
**b-Naphthol Picrate.** C_10H_8O + C_6H_5O_7^-N_3; orrn-red needles; mp 155–57°; expls at about 469°  (Beil 6, 640, (312) & [597])  
**Phenantheone Picrate.** C_{14}H_{10}^+ + C_6H_5O_7^-N_3; golden yel needles; mp 143–45°; expls at 478°  (Beil 6, 273, (132) & [261])  
**Pyridine Picrate.** C_5H_5N^+ + C_6H_5O_7^-N_3; golden yel needles; mp, 165–66°; expls at 432°  (Beil 20, 208)  
**Quinidine Picrate.** Expls at 280°  (R.J. Datta & N.R. Chatterjee, JCS 115, 1008 (1919))  
**Semicarbazide Picrate.** Expls at 474°  (R.J. Datta & N.R. Chatterjee, JCS 115, 1008 (1919))  
**Strychnine Picrate.** Explodes at about 290°  (R.J. Datta & N.R. Chatterjee, JCS 115, 1008 (1919))  
**o-Toluidine Picrate.** Pale yel crysts; mp 185°; expls at about 400°  (Beil 12, [433])  
**Urea (or Carbamide) Picrate.** CH_4ONO_2 + C_6H_5O_7^-N_3; yel needles; mp 142° (decomp); expls at about 489°  (Beil 6, 279 & R.J. Datta & N.R. Chatterjee, JCS 115, 1008 (1919))  

**Picrate Whistles.** According to Davis (Ref 1), an intimate mixt of finely powdered K picrate and K nitrate (60/40 by wt), rammed tightly into paper or bamboo tubes from 1/4" to 3/4" in diameter, burns with a loud whistling sound.  
In WWII, the Germans used picrate whistles as a psychological adjunct to bombs, and they also used pyrotechnic whistles as gas alarms  
Because the above mixt is extremely sensitive to shock and dangerous to handle, non-picrate whistle compns such as those contg gallic acid and K chloride are currently utilized (Ref 2)  
**Refs:** 1) Davis (1943), 72–73  2) Ellern (1968), 183 & 376–77  

**Picratol.** A mixt of TNT/Ammonium Picrate (48/52% by wt) developed in the USA during WWII to replace pure Ammonium Picrate (Explosive D) in AP and SAP projectiles and bombs. OB TO CO_2 –63%, to CO –19%  
Prior to WWII, armor-piercing projectiles were press-loaded with Explosive D. This required the application of pressures of the order of 10,000 to 12,000psi to successive increments of the charge and was a slow and expensive operation. The development of armor-piercing bombs necessitated the use of an insensitive expl that could be melted loaded; and for this reason,
Picratol was developed

Molten TNT has little or no solvent action on Explosive D, and consequently, cast Picratol consists essentially of a physical mix of crystals of the two explosives. Its density is 1.61 to 1.63 g/cc, and this permits a weight of charge almost equal to that of Explosive D pressed under 10,000 to 12,000 psi. Picratol has the solubility and reactivity characteristics of its ingredients. It is hygroscopic to the extent of only 0.02% when exposed to an atm of 90% RH at 30°C.

Preparation. Picratol is manufactured by heating TNT to above 90°C in a steam-jacketed melting kettle equipped with a stirrer. The Explosive D is added slowly, without preheating, with continuous agitation; and this is continued for a short time after all the Explosive D has been added. The thick slurry is allowed to cool to about 85°C before being cast into ammo components. Like molten TNT, it undergoes marked contraction in volume on solidification; but this is much less than in the case of TNT.

Sensitivity. The standard small scale impact tests indicate Picratol to be as sensitive to impact as TNT, rather than Explosive D, and large scale impact tests of cast charges confirm this. Friction pendulum tests show no difference between Picratol, TNT, and Explosive D, with respect to sensitivity to friction. When subjected to the rifle bullet impact test, Picratol burns in about 40% of the trials, but undergoes no detonation. Explosive D burns in about 30% of the trials. The explosion test value (5 sec) of Picratol (285°C) is less than that of Explosive D (318°C), and much less than that of TNT (475°C). Picratol is as insensitive to initiation as Explosive D, having a minimum detonating charge of 0.06 g of Tetryl. The overall sensitivity of Picratol, therefore, is not greater than that of Explosive D.

Explosive Properties. Picratol is only 94% as brisant as TNT, as judged by the sand test, but the plate dent test indicates the two to be equally brisant, and the fragmentation of shot charges show Picratol to be 102% as brisant as TNT. The rate of detonation of cast Picratol (unconfined charge, 1.63 g/cc, 1.00" diam) is 6970 m/sec, 101% that of cast TNT. Picratol and TNT are of equal power, as measured by the Ballistic Pendulum test, and have equal blast effects.

Stability. The stability of Picratol is very slightly less than that of either TNT or Explosive D, as measured by Vacuum Stability tests at 100°C (0.37 cc/40 hrs), 120°C (0.68 cc) and 150°C (0.70 cc). These tests results may be considered to indicate slight reaction between the Explosive D and the molten TNT ingredients at the elevated temps of the tests. At ordinary temps there is no evidence of such reaction, and Picratol appears to be of the same high order of stability as its ingredients.

Analytical. The compn of Picratol can be determined by extracting a weighed sample with cold eth that has been sated with Explosive D. The residue is dried and weighed, and this and the loss in wt are calc'd to % of Explosive D and TNT, respectively.


Picric Acid (PA; listed as 2,4,6-Trinitrophenol in CA since 1972; Mélinite in Fr; Melinit in Russ, Lyddit in Eng; Granatfullung or Sprengkorper 88 in Ger; Peritt in Ital; Picinit in Span, Ekrafit in Aust; TNF in Pol; Shimoz in Jap)

\[
\text{O}_2\text{N} - \text{NO}_2
\]

MW 229.11, N 18.34%, OB to CO₂ −45%, yel rhomb crystals, mp 122°C, d 1.76 g/cc. In recent years PA has fallen out of favor as an expl. Consequently, modern literature on PA is not voluminous and this article of necessity draws heavily upon older literature. The article is divided into the following sections: I. Historical; II. Physical Properties, Solubility and Toxicity; III. Thermochemical Data; IV. Chemical Properties; V. Specifications & Analytical; VI. Uses; VII. Preparation; VIII. Explosive Characteristics; and IX. References.

1. Historical. PA is probably the earliest known nitrophenol. According to Urbanski (Ref 35) it is mentioned in the alchmical writings of Glauber as early as 1742. Glauber reacted nitric acid with wool or horn and isolated PA in the
form of Pb or K picrates. A few decades later, Woulfe (Ref 1) prepared PA by treating indigo with nitric acid. In 1783, Hausmann (Ref 2) showed that PA behaves like an acid. Other early experimenters (Refs 3–5) obtained PA by nitratating various organic substances such as silk, natural resins, etc. Marchand (Ref 6) assigned it the empirical formula of $C_{12}H_8N_6O_4$, which is exactly double the actual formula. The correct constitution of Picric Acid was determined by Laurent (Ref 7) in 1841. He prepared it by reacting phenol with nitric acid. He was also able to isolate dinitrophenol formed in an intermediate stage of the nitration. A further improvement in the method of preparation of Picric Acid from phenol was its sulfonation prior to nitration, described by Schmidt and Glutz (Ref 8).

Some of the authors had drawn attention to the explosive character of Picric Acid salts, but it was not until 1830 that Welter (Ref 3) suggested the possibility of using picrates as expls. At that time Picric Acid was prepared solely by the action of nitric acid on indigo. Marchand (Ref 6) expressed the view, which proved to be true, that it was aniline, formed as an intermediate product in the process of decomposition of indigo, silk and other organic matter, that yielded Picric Acid under the influence of nitric acid.

According to Urbanínski (Ref 35, p 473): “In the second half of the nineteenth century, Picric Acid was very widely used as a fast dye for silk and wool. The first definite suggestions as to the application of Picric Acid for the manufacture of explosives go back to the early second half of the nineteenth century. They referred to the application of Picric Acid salts, as by then the explosive properties of picrates were already well known. Thus, for example, Desagnolle (Ref 17) suggested K picrate, and Brugère (Ref 9) ammonium picrate as propellants, while in 1871 Abel (Ref 10) proposed ammonium picrate as a high explosive. At that time K picrate was already being used in Great Britain and in the US for filling shells.

The view then prevailed, supported by such an authority as Abel, that Picric Acid itself is not an explosive, but only its salts are. Nevertheless in 1873 Spengel (Ref 11) proved that Picric Acid could be brought to explosion by a detonator and Turpin (Ref 12) proposed applying this property of Picric Acid by utilizing it for filling shells. In Russia methods of preparation of Picric Acid and using it as a shell filling were worked out near 1894 by Panpushko (Ref 26). Eventually Picric Acid was accepted all over the world as the basic high explosive for military uses.”

However during the present century TNT has been continuously replacing PA as the main military explosive. To some degree this change was accelerated by the acidic character of Picric Acid and its corrosive action on metals, resulting in the formation of salts sensitive to impact and friction. Moreover, because of its relatively high sensitiveness to impact, Picric Acid by itself is unsuitable for filling certain special purpose ammo, for example for armor piercing shells.

II. Physical Properties, Solubility and Toxicity.

PA crystallizes in colorless yellowish needles or lamellae of the orthorhombic-bipyramidal system. It sublimes above its mp, and its vapor press is 2 mm Hg at 195° and 50 mm Hg at 255° (Ref 48). The specific gravity of liquid PA is 1.59 g/cc at 124° and 1.51 g/cc at 170°. In satd air at 32° PA picks up 0.37% moisture in 48 hours (Ref 35). According to Dautriche (Ref 14), PA packing density varies with loading pressure as follows:

<table>
<thead>
<tr>
<th>Pressure, kg/cm²</th>
<th>Average density, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>1.315</td>
</tr>
<tr>
<td>685</td>
<td>1.480</td>
</tr>
<tr>
<td>1375</td>
<td>1.614</td>
</tr>
<tr>
<td>2060</td>
<td>1.672</td>
</tr>
<tr>
<td>2750</td>
<td>1.714</td>
</tr>
<tr>
<td>3435</td>
<td>1.731</td>
</tr>
<tr>
<td>4125</td>
<td>1.740</td>
</tr>
</tbody>
</table>

The IR spectrum of PA is given by Levitsky et al (Ref 37).

PA is somewhat sol in w and more sol in acids. It also dissolves in a variety of org solvents. According to Dolinsky (Ref 13), its soly in w is shown in Table 1.
Table 1
Solubility of Picric Acid in Water

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Content of Picric Acid, g in 100g of solution</th>
<th>in 100g of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.67</td>
<td>0.68</td>
</tr>
<tr>
<td>10</td>
<td>0.80</td>
<td>0.81</td>
</tr>
<tr>
<td>20</td>
<td>1.10</td>
<td>1.11</td>
</tr>
<tr>
<td>30</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>40</td>
<td>1.75</td>
<td>1.78</td>
</tr>
<tr>
<td>50</td>
<td>2.15</td>
<td>2.19</td>
</tr>
<tr>
<td>60</td>
<td>2.77</td>
<td>2.81</td>
</tr>
<tr>
<td>70</td>
<td>3.35</td>
<td>3.47</td>
</tr>
<tr>
<td>80</td>
<td>4.22</td>
<td>4.41</td>
</tr>
<tr>
<td>90</td>
<td>5.44</td>
<td>5.72</td>
</tr>
<tr>
<td>100</td>
<td>6.75</td>
<td>7.24</td>
</tr>
</tbody>
</table>

In sulfuric acid the amount of PA dissolved goes thru a min at about 18% acid (Ref 15) (Table 2)

Table 2
Solubility of Picric Acid in H₂SO₄

<table>
<thead>
<tr>
<th>H₂SO₄ concen %</th>
<th>Picric Acid content in 100g of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18°C</td>
</tr>
<tr>
<td>0</td>
<td>1.184</td>
</tr>
<tr>
<td>2.3</td>
<td>0.230</td>
</tr>
<tr>
<td>4.7</td>
<td>0.142</td>
</tr>
<tr>
<td>10.0</td>
<td>0.091</td>
</tr>
<tr>
<td>18.0</td>
<td>0.079</td>
</tr>
<tr>
<td>25.5</td>
<td>0.092</td>
</tr>
<tr>
<td>50.5</td>
<td>0.429</td>
</tr>
<tr>
<td>69.7</td>
<td>0.282</td>
</tr>
<tr>
<td>87.9</td>
<td>1.161</td>
</tr>
<tr>
<td>97.4</td>
<td>7.531</td>
</tr>
<tr>
<td>100.0</td>
<td>10.180</td>
</tr>
</tbody>
</table>

Drucker (Ref 20) gives the following PA solubilities in nitric acid (Table 3)

Table 3
Solubility of Picric Acid in Nitric Acid

<table>
<thead>
<tr>
<th>HNO₃ concentration in mole/²</th>
<th>Picric Acid concentration in mole/²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>0.05327</td>
</tr>
<tr>
<td>0.00635</td>
<td>0.05095</td>
</tr>
<tr>
<td>0.02564</td>
<td>0.04281</td>
</tr>
<tr>
<td>0.05166</td>
<td>0.03493</td>
</tr>
<tr>
<td>0.0872</td>
<td>0.02604</td>
</tr>
</tbody>
</table>

In organic solvents the solubility of PA was measured by Urbanski (Ref 35) (Table 4)

Table 4
Solubility of Picric Acid in Organic Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp °C</th>
<th>Amount of solvent</th>
<th>Amount of PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl alcohol</td>
<td>25</td>
<td>100 ps</td>
<td>7.452 ps</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>13</td>
<td>100 ps</td>
<td>1.08 ps</td>
</tr>
<tr>
<td>Ethyl ether (water satd)</td>
<td>13</td>
<td>100 ps</td>
<td>4.00 ps</td>
</tr>
<tr>
<td>Benzene</td>
<td>6</td>
<td>100 ps</td>
<td>3.50 ps</td>
</tr>
<tr>
<td>Benzene</td>
<td>15</td>
<td>100 ps</td>
<td>5.9 ps</td>
</tr>
<tr>
<td>Toluene</td>
<td>20</td>
<td>100 ml soln</td>
<td>12.0 g</td>
</tr>
<tr>
<td>Amyl alcohol</td>
<td>20</td>
<td>100 ml soln</td>
<td>1.755 g</td>
</tr>
</tbody>
</table>

and by Duff & Bills (Ref 21) (Table 5)

Table 5
Solubility of Picric Acid

<table>
<thead>
<tr>
<th>% of organic component of the soln</th>
<th>Methyl alcohol</th>
<th>Ethyl alcohol</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>30</td>
<td>2.4</td>
<td>3.1</td>
<td>9.5</td>
</tr>
<tr>
<td>60</td>
<td>7.1</td>
<td>10.5</td>
<td>46.7</td>
</tr>
<tr>
<td>80</td>
<td>13.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>81</td>
<td>13.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>85</td>
<td>13.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90</td>
<td>12.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>8.0</td>
<td>-</td>
<td>43</td>
</tr>
</tbody>
</table>

PA forms eutectics with TNT and 2,4,6-trinitroxyylene. The former contains about 33% PA and melts at 59°, while the latter contains about 78% PA and melts at 106° (Ref 35)
Toxicity. Picric Acid is more toxic than the nitro derivatives of toluene, xylene or naphthalene. It is, however, much less toxic than nitro derivatives of benzene.

According to Lazarov (Ref 27) a single lethal dose for a cat is 0.5g/kg of its weight. A daily dose of 0.05–0.2g/kg causes death after 9 days.

Saladini (Ref 15a) pointed out that small doses of PA cause no ill-effects in man.

Koelsch (Ref 16), based on observation of 1200 workers engaged in handling PA, described the symptoms of poisoning as follows: a yellow coloration of unprotected parts of the skin and hair, irritation of the mucous membranes and of the upper parts of the respiratory tract and the digestive tract. In addition, a constant bitter taste and a lack of appetite appear.

Similar results of observations, carried out at the Institute of Occupational Diseases in Leningrad, were reported by Matusevich (Ref 19).

Lebedev (Ref 22) described the signs of mild poisoning by Picric Acid as follows: Yellow coloration of the skin, the teeth, the saliva and nasal mucous, bitter taste, lack of appetite, occasionally nausea and vomiting. A decrease in the acidity of the gastric juice is also possible, as well as conjunctivitis, irritation of the upper respiratory tract and of the middle ear. Instances of perforation of the nasal wall are also known. In more severe cases an intense headache appears, as well as abnormally high temp, dizziness, spasms, disturbances of the digestive organs, anemia and more rarely kidney trouble. In women menstrual disturbances may occur. More or less severe eczema may also appear.

According to Nawrooki and his co-workers (Ref 23), a concn of Picric Acid in air amounting to 1–17.5mg/m³ may cause severe poisoning after six hours’ exposure.

Koelsch (Ref 16) suggested the following protective measures when working with PA: adequate ventilation to prevent the accumulation of PA dust, protective clothing including gloves and head coverings to cover as large an area of the skin as possible, and washing the face and hands and rinsing the mouth before eating. Taking meals in working quarters should be forbidden. Workers should be subjected to medical inspection at regular intervals.

### III. Thermochemical Data

The std heat of formation of PA is $-51.3$ kcal/mole (Ref 41). The heat of fusion is $4.7$ kcal/mole (Ref 48) and the heat of vaporization is $21.0$ kcal/mole (Ref 25). Taylor & Rinkenbach give the following variation of specific heat with temp (Ref 18):

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Specific heat, cal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.234</td>
</tr>
<tr>
<td>20</td>
<td>0.250</td>
</tr>
<tr>
<td>40</td>
<td>0.266</td>
</tr>
<tr>
<td>60</td>
<td>0.282</td>
</tr>
<tr>
<td>80</td>
<td>0.300</td>
</tr>
<tr>
<td>100</td>
<td>0.318</td>
</tr>
<tr>
<td>120</td>
<td>0.337</td>
</tr>
</tbody>
</table>

There is disagreement about the coefficient and heat conductivity of PA. Belyaev & Matyshko give it as $2.4 \times 10^{-3}$ cgs units at 1.7g/cc (Ref 24), while H.H. Licht's value (Ref 44) is $6.2 \times 10^{-4}$ cgs units at 1.41g/cc.

Urbanski (Ref 35) gives the total heat of nitration as $-917.4$ kcal/kg of phenol.

### IV. Chemical Properties & Thermal Decomposition

Most of the chemistry of PA is determined by its acidic nature. It is a strong acid whose ionization constant of $1.6 \times 10^{-1}$ (Ref 31) makes it comparable in acid strength to pyrophosphoric acid and trichloroacetic acid. PA readily forms salts with bases and esters with alcohols. The salts are known as Picrates. Many of them are expl and will be described in a separate article in this Vol. The esters are phenol ethers, eg, Trinitroanisole (see Vol 1, A450-L).

Like other polynitroaromatic compounds, Picric Acid readily forms addition products with aromatic hydrocarbons. This behavior is especially pronounced in PA. Addition comnds with phenols, aromatic ketones, acids and even with nitro comds are also known.

Urbanski (Ref 35) lists the following addition comds formed by Picric Acid with other sub- stances in a 1:1 mole ratio:
Second component | Melting points, °C
---|---
Anthracene | ca 141 (non uniform melting)
Benzene | 84
Fluorene | 84
Naphthalene | 150
Phenol | 85
Resorcinol | 100
Pyrocatechol | 124
Guaiacol | 88.6
α-Cresol | 89.8
p-Cresol | ca 65.6 (non uniform melting)
Thymol | 96.8
β-Naphthol | 145.8
Triphenylcarbinol | 138.5
Acetophenone | ca 50 (non uniform melting)
Benzophenone | 27 (readily dissociates)
Cinnamic acid | 106.5

According to Urbański (Ref 35), Hantzsch proposed that PA exists in two forms: a colorless form (I) and two equivalent colored quinoid forms (II):

Salt formation generally favors the quinoid form and these salt solns are usually brightly colored. Presence of strong acids favors the colorless phenol form. Because of these color changes, nitrophenols have been used as indicators in acid-base titrations.

PA exerts an inhibiting action on free radical polymerizations. Bartlett et al (Ref 28) ascribe this to the following reactions:

**Thermal Decomposition.** The definitive study of the thermal decompn of PA was made by Andreev and Liu Pao-Feng (Ref 34). They followed the decompn of liq PA manometrically over the temp
range of 183–270°. They also examined the decomp of PA vapor at 290°. The decomp of the liq is complex and may proceed in as many as five different stages. If the total pressure in the reaction vessel is kept low (low m/V, ie, a small PA mass m in a large vessel of vol V) there is a long induction period at 183°. This induction period can be appreciably shortened by increasing m/V. There is no apparent induction period for decomp at 230° or above. Where induction is observed it is followed by an accelerated decomp stage which goes over into an essentially first order decomp rate. The final stages of decomp may be autocatalytic. At the higher temps most of the decomp is nearly first order.

In the vapor state PA decomps is much slower than for the liquid. Above an initial vessel pressure of 110mm Hg the decomp is nearly first order. The decomp rate is strongly enhanced by the presence of added glass surfaces.

From the variation of reaction rate with temp in the region where first order kinetics hold, the authors calculate an activation energy of 38.6 kcal/mole and a pre-exponential factor of 4 x 10^{11} sec^{-1}. These Arhenius parameters are fairly similar to those of TNT (see article on Kinetcs in Vol 7, K6-R ff).

Recently Boguslavskaya et al (Ref 49), on the basis of ESR studies, have suggested that thermal decomp of PA proceeds via the following free radical intermediates:

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{=NO}^- \\
\text{NO}_2 & \quad \text{or}
\end{align*}
\]

According to Rosen & Dacons (Ref 39) PA dissolved in trinitrobenzene (5 mole % soln) has an initial gas production of 2.8 cc at NTP/hour at 210° in a vacuum stability test. For comparison, at nearly identical conditions TNT gives 0.6 cc gas/hour at 230°

V. Specifications and Analytical. According to JAN-A-187 (1945), section E, military PA has to meet the following specifications:

- **Color** – White to yellow
- **Granulation** – Min 99.5 percent thru 1410 mi-
- **Cron (No 14) US Standard sieve**
  - **Solidification point** – Min 120.0°
  - **Moisture—when purchased dry** – max 0.20 percent; **when purchased wet** – max 22.0 percent
  - **Ash** – Max 0.1 percent
  - **Insoluble matter** – Max 0.1 percent
  - **Acidity — total sulfuric acid** – max 0.1 percent; **nitric acid** – none
  - **Lead** – max 0.004 percent

Analytical. A qualitative test for PA depends on its reaction with aq KCN to form a red colored salt, the so-called “isopurpuric acid”. The reactions involved in this test are still in doubt (see Ref 35, p 492). PA is one of the few trinitroaromatics that does not produce a reddish coloration with strong alkalis (Ref 46). It has an IR band characteristic of sym trinitroaromatics, but because of its acidic nature the band is shifted from 9.25 μm to about 9.35 μm (Ref 46). The general method of determining N content of nitroaromatics by titrametric chloride reduction and titration of the added excess by ferric chloride is presumably applicable to PA (Ref 46). Hansson (Ref 33) developed a thin-layer chromatographic method for PA and other expls. The expls, as 1% solns in acetone, are put on silica gel layers using benzene or petr ether carriers.

VI. Uses. During the latter part of the nineteenth century and the early part of the present century, PA was widely used as the main expl charge of projectiles and bombs. This is no longer true. Indeed PA per se is hardly used as an expl. Its current limited expl-related use is primarily in the preparation of Explosive D (Ammonium Picrate) and Lead Picrate. It also finds some use as an intermediate in the manuf of dyes. There is some patent literature on the use of PA as a catalyst for polymerizations. For example, PA is claimed as catalyst in polybutadiene polymerizations (Ref 40), and for the prep of an isobutylene-5-methyl-1,3,6 heptatriene copolymer (Ref 38).

VII. Preparation. There are two industrial methods of manuf PA: 1) nitration of Phenol; 2) nitration of dinitrophenol prep by hydrolysis of chlorodinitrobenzene

Nitration of phenol. This is a two stage process. First, phenol is sulfonated and the sul-
fonates are then nitrated with nitric acid. The intermediate sulfonation step is necessary because direct nitration of phenol yields undesirable oxidation and condensation side products. Furthermore the two stage process permits the nitration step to be carried out without use of excess acid. Thus the small amount of spent acid need not be recovered, and can be discharged into the drainage system. This is an advantage since the spent acid does contain PA. Production of appreciable amounts of spent acid would entail some rather formidable PA recovery problems. Moreover, PA is fairly volatile in sulfuric acid solns and this presents the risk of escaping and possibly forming dangerous metal salts upon condensing on metal parts or equipment.

The sulfonation steps are carried out at around 100\(^\circ\)C, using 4 to 4.5 moles of sulfuric acid per mole of phenol. The reaction proceeds thru an intermediate sulfuric acid ester:

\[
C_6H_5OH + H_2SO_4 \rightarrow SO_2O-C_6H_5 + H_2O
\]

which is then converted to the ortho & para phenolsulfonic acids:

\[
\begin{align*}
OH & \quad \text{OH} \\
\text{SO}_2\text{H} & \quad \text{SO}_3\text{H}
\end{align*}
\]

According to Urbanski (Ref 35): “At room temperature the conversion proceeds slowly, whereas it occurs rapidly on heating. The higher the temperature, the more \(p\)-isomers are formed. At 90–100\(^\circ\)C phenoldisulphonic acid is also formed:

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{SO}_3\text{H} & \quad \text{SO}_3\text{H}
\end{align*}
\]

Its presence is advisable, as later it will facilitate the nitration process.”

The second stage of this process consists of nitration of the phenol sulfonic acids with concd nitric acid. The overall process is represented diagrammatically as:
If sulfonation is carried out at a low temp, nitric acid of higher concn should be used or a higher temp should be maintained during the nitration. The latter must, of course, be kept within safety limits. Apart from this, higher temps naturally favor undesirable side reactions (eg, oxidation)

Nitrilation of dinitrophenol. This is a multistage process. First chlorobenzene is nitrated to chlorodinitrobenzene as shown schematically below:

The dinitrobenzenes are then hydrolyzed at about 100°C in a 7% Na hydroxide soln. The Na-dinitrophenate thus formed is acidified with 30% sulfuric acid to produce dinitrophenol which is nitrated with mixed acid (0–5% water content) to form PA.

Recently it has been claimed (Ref 42) that PA may be prep'd by nitrosating phenol with Na nitrate and oxidizing the resulting nitrosophenol with nitric acid.

VIII. Explosive Characteristics. Picric Acid is generally considered to be a relatively "insensitive" but brisant expl. On a qualitative sensitivity scale of comparing common expls, PA would be judged to be more sensitive than TNT but appreciably less sensitive than Tetryl. Its power and brisance are also similar to those of TNT (112% TNT in the Ballistic Mortar; 101% of TNT in the Trauzl Block and 107% in the plate dent test (Ref 48). In this section we will consider the steady detonation parameters, initiation characteristics and potential hazards of PA.

A. Steady Detonation Parameters. As already mentioned, PA is an expl that is currently out of favor. Consequently there are relatively few modern data on its detonation characteristics

Detonation Velocity: Baum et al (Ref 31b, p 352) gives the following tabulation of packing density \( \rho \) vs deton vel D:

<table>
<thead>
<tr>
<th>( \rho ) (g/cc)</th>
<th>D (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.97</td>
<td>4965</td>
</tr>
<tr>
<td>1.32</td>
<td>6190</td>
</tr>
<tr>
<td>1.41</td>
<td>6510</td>
</tr>
<tr>
<td>1.62</td>
<td>7200</td>
</tr>
<tr>
<td>1.70</td>
<td>7480</td>
</tr>
</tbody>
</table>

These values agree reasonably well with those obtained from the following formula of Cook (Ref 31a, p 45):

\[
D = 5.255 + 3045 (\rho - 1.00) \text{ m/sec}
\]

Baum (Ref 31b, p 349) also gives the following tube diameters, \( d_m \), at which D approaches its max (hydrodynamic) value:

\begin{align*}
\text{PA grain size (mm)} & \quad \rho \text{ (g/cc)} & \quad d_m \text{ (mm)} \\
0.1–0.75 & 0.95 & 17 \\
\text{"small" (sic)} & 0.95 & 11
\end{align*}

Johansson & Persson (Ref 45, p 41) show the results of Parisot & Lafitte (1938) in the D vs diameter curves in Fig 1 (expls other than PA also shown). There appears to be some dis-

Fig 1
Detonation Velocity vs Charge Diameter
agreement between these data and those of Baum in that Parisot & Lafitte's $d_m$ is rather higher than that of Baum

Critical diameter, $d_c$, is the diameter below which steady detonation is impossible. For PA, Baum (Ref 31b, p 349) and Andreev & Belyaev (Ref 32, p 289) give:

<table>
<thead>
<tr>
<th>Grain size (mm)</th>
<th>$\rho$ (g/cc)</th>
<th>$d_c$ (mm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1–0.75</td>
<td>0.95</td>
<td>9.0</td>
<td>31b</td>
</tr>
<tr>
<td>&quot;small&quot;</td>
<td>0.95</td>
<td>5.5</td>
<td>31b</td>
</tr>
<tr>
<td>0.01–0.05</td>
<td>0.8</td>
<td>2.1–2.3</td>
<td>32</td>
</tr>
<tr>
<td>0.05–0.07</td>
<td>0.7</td>
<td>3.6–3.7</td>
<td>32</td>
</tr>
</tbody>
</table>

Detonation Products & CJ Parameters. Mader (Ref 33a) computed the following detonation product compn for 1.76g/cc and 1.00g/cc densities:

<table>
<thead>
<tr>
<th></th>
<th>1.76g/cc</th>
<th>1.00g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2.661</td>
<td>1.310</td>
</tr>
<tr>
<td>CO</td>
<td>0.179</td>
<td>2.970</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.499</td>
<td>1.409</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.500</td>
<td>1.496</td>
</tr>
<tr>
<td>C$_{solid}$</td>
<td>3.160</td>
<td>1.713</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td>0.065</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>0.008</td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td>0.006</td>
</tr>
</tbody>
</table>

These calcns also provide the following steady detonation (CJ) parameters (Q is the heat of detonation):

<table>
<thead>
<tr>
<th></th>
<th>1.76g/cc</th>
<th>1.00g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{m/sec}$</td>
<td>7680</td>
<td>5545</td>
</tr>
<tr>
<td>Press (kbar)</td>
<td>265</td>
<td>88</td>
</tr>
<tr>
<td>Q (kcal/g)</td>
<td>1.27</td>
<td>1.02</td>
</tr>
<tr>
<td>Spec Vol (cc/g)</td>
<td>0.423</td>
<td>0.714</td>
</tr>
</tbody>
</table>

Aside from the expected agreement between computed and expnl D, there is only one other check on the validity of these calcns. In Ref 30, Q for PA at 1 g/cc is given as 1.0kcal/g, which is in excellent accord with the Q value in the above tabulation.

Combustion. Like many other granular expls, PA will burn quite stably with an increase in burning rate as the ambient pressure is increased. Andreev (Ref 34, p 377) gives the following expression for the mass burning rate of PA:

$$u_m = 0.14 + 0.00805P$$

where $u_m$ is in g/cm$^2$ and $P$ is in kg/cm$^2$. This expression is claimed to hold for ambient pressures of 25 to 950 atm.

The same author (Ref 32) nevertheless states that PA packed at about 60% of its theoretical max density into sealed bombs (equipped with variable rupture disks) detonates partially at 500–700 atm ambient pressure and detonates fully at 1200 atm. Possibly the mass burning rate experiments were made at a much lower loading fraction (vol of PA/vol of container) than the bomb experiments. However Afonina et al (Ref 43) claim that PA at 1 g/cc shows little tendency toward DDT (deflagration-to-detonation transition) in steel tubes that can withstand 5–12kb of pressure.

B. Initiation Characteristics

Minimum priming charge is the weight of a standard initiating expl required to produce stable detonation in the test expl. For PA the min priming charge is 0.24g of Lead Azide according to Ref 48, but according to Andreev & Belyaev (Ref 32, p 447) it is only 0.08 or 0.03g for pressed charges passing thru 2500 holes/cm$^2$ or 10,000 holes/cm$^2$ sieves.

Heat Sensitivity. Henkin & McGill (Ref 29) report the following explosion temperatures for PA:

<table>
<thead>
<tr>
<th>Temp $^\circ$C</th>
<th>Time to explosion (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.5</td>
</tr>
<tr>
<td>315</td>
<td>5.5</td>
</tr>
<tr>
<td>277</td>
<td>26.3</td>
</tr>
<tr>
<td>267</td>
<td>50.3</td>
</tr>
<tr>
<td>260</td>
<td>failed</td>
</tr>
</tbody>
</table>

These data were obtained for 25mg PA samples contained in small-diameter, thin-wall copper tubes which were partially submerged into a heat bath.

Andreev & Belyaev (Ref 32, p 476) state that PA ignites in 5 secs at 322$^\circ$, which is in reasonable accord with the above. They also report that for "slow" heating (20$^\circ$/min) PA ignites at 300–310$^\circ$ (Ref 32, p 475).

Impact Sensitivity. In the Bureau of Mines impact test (see Vol 7, 136–40) PA shows a 50% height of 65–93cm (Refs 30 & 48). In the Picatinny impact test it has a 13-inch height (Ref 48). On a relative scale (which is the only really significant scale) PA is thus somewhat less impact sensitive than TNT. This is also borne out by the results of Afanasev & Bobolev (see Vol 7, 151) who obtain the following critical stresses for impact initiation of PA & TNT respectively: 9.5 x 10$^3$kg/cm$^2$ and 11 x 10$^3$kg/cm$^2$.

According to Andreev & Belyaev (Ref 32, p 471) PA shows some slight sensitivity to friction in that it produces a weak burning odor under con-
ditions where Tetryl crackles and Lead Picrate expls.

**PROJECTILE SENSITIVITY.** Andreev & Belyaev (Ref 32, p 473) showed that PA packed in wooden crates detonates if impacted by a 4g projectile moving at greater than 400m/sec. In the rifle bullet sensitivity test 0% explosions, 60% partials and 40% combustions were observed for PA (Ref 48)

Vasilev (Ref 36) impacted various explosives with steel plates and followed events with a framing camera. PA at 1.59g/cc impacted with a 0.3mm thick steel plate at 430m/sec showed only deflagration and no expls. Initially the burning rate was low but reached 600m/sec in about 65 microseconds after impact

**C. POTENTIAL HAZARDS.** The main danger of accidental expln of PA appears to be in fires. There appears to be uncertainty if expls result if PA burns out of contact with metals. On p 494, Urbanski (Ref 35) states:

"Picric Acid melts prior to burning giving a sooty flame. The heat of fusion lowers the temperature of the layer adjacent to the burning one, so the substance may either stop burning or continue to burn only gently. In large quantities, burning of Picric Acid may proceed slowly, especially when it is spread over a larger area. If, however, the material is concentrated in a small area or when it is in a confined space, explosion may occur. Burning Picric Acid containing metal picrates may result in explosion. Similarly a potential danger exists when burning Picric Acid is in contact with metals, since in the molten state it forms picrates which may initiate explosion. This depends largely on the metal: lead, iron, copper should be considered particularly dangerous."

However, on p 530 Urbanski says:

"If Picric Acid is free from picrates, its burning, even in large quantities, does not present any risk of explosion. A case is known (in the USA) when 100 tons of Picric Acid caught fire. It burned relatively smoothly although the flame attained a height of 10-15m and a characteristic loud whistling noise was heard. Slight explosions were observed only when roof fragments fell into the burning mass, causing blasts from a violent eruption of confined gases."

Several violent explosions have occurred when PA burned in contact with metals. Urbanski (Ref 35, p 530) refers to three such expls:

"A violent explosion of Picric Acid in a Manchester factory in 1887 was ascribed to the formation of picrates. Burning, molten Picric Acid flowed down onto lithopone, forming lead picrate which in consequence caught fire. The latter, being an initiator, detonated and caused the Picric Acid to detonate.

A fire, followed by an explosion at Huddersfield in 1900 was also caused by detonation of iron picrate (presumably Fe++). The iron picrate had been formed on the surface of steam pipes located in the Picric Acid drier shop. It ignited when a plumber, unaware of the fact, struck one of the pipes with a hammer. The flame spread along the pipe and set the drying Picric Acid on fire.

In a French factory streaks of Picric Acid had been formed alongside a narrow gauge railway. As the soil beneath was calcareous, calcium picrate formed which, having dried up in the summer, was ignited by friction or a blow, spreading flames all over those parts of the factory marked with calcium picrate streaks."

As was mentioned in the Picric Acid (PA) article, straight PA was used extensively for cast and press loading of various projectiles. Fr, Engl and Japan appear to have used PA more than any other HE almost to the beginning of WWII. However, the use of straight PA is not always advisable because of the following disadvantages: 1) a high mp, 120-220, which makes cast loading a fairly dangerous operation, 2) corrosive action on metals, except for Al and Sn.; and 3) instability in storage at tropical temps

The first of these disadvantages can be overcome by adding selected nitrocompds to PA which have the property of lowering its mp. The following table, taken from p 14 of Ref 2, shows the mp’s of a few characteristic mixts of this nature, the proportions being molecular.

One of the most common addition compds to PA to lower its mp was trinitro-m-cresol, eg, in the Fr expl Cresylite. Other compds used were DNPh, DNT, DNM, MNN, MNPPh, TNT, TNm-X, DNB, TNB, etc.

An ingenious method for the prep of cast exps contg 90-95% PA and 5-10% nitrocompds, such as TNT, TNc, TNB, TNX, DNB, DNT, DNPh, etc, was patented in Ger in 1892 [GerP 69897 (1892)]. It consisted of placing a mixt of PA with 5-10% of the nitrocomp in mounds of the desired shape, and heated for a short time to a temp slightly above the mp of the nitrocomp, with or without the employment of pressure. The nitrocomp melts and cements the PA crystals together so that when cooled the mixt forms a hard mass. It was claimed that the manuf of such charges was absolutely safe, and that they possessed no dangerous properties in use or transport (Ref 2, p 697).

In addition to adding nitrocompds to PA to lower its mp, other substances could be added, such as oxidizers (K nitrate, Na nitrate, AN, Ba nitrate, Pb dioxide, Amm dichromate, K chlorate, K perchlorate, etc), fuels (such as sawdust, S, starch, lignite, charcoal, tar, naphthalene, etc), picrates, NG, NC resins, etc. Some exps even contained fuming acid, eg, Emmens Acid and Emmensite.

The following is a selected list of exps, covered in this Encycl in detail under their alphabetical listing, contg PA or picrates as the
Table 1

Nitrocompound Addition to Picric Acid for Melting Point Lowering

<table>
<thead>
<tr>
<th>Proportion</th>
<th>Nitrocompounds and their Melting Points in °C</th>
<th>Melting Point of the Mixture in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>PA (122°) + Nitronaphthalene (61°)</td>
<td>49°</td>
</tr>
<tr>
<td>1:1</td>
<td>PA (122°) + TNT (80.2°)</td>
<td>47°</td>
</tr>
<tr>
<td>1:1</td>
<td>PA (122°) + Trinitroresol (107°)</td>
<td>70°</td>
</tr>
<tr>
<td>2:1</td>
<td>PA (122°) + Trinitroresol (107°)</td>
<td>78°</td>
</tr>
</tbody>
</table>


Picric Nitrogelatine (Nitrogelatine Picrique in Fr). A gelatinous expl compd patented in Ger in 1887, prepd by mixing 10p of NG with 1 p of PA and gelatinizing the resulting soln with a small amt of collodion cotton. Such materials as flour, starch, nitrates, chlorates, perchlorates, etc, could be added to this jelly

Ref: Cundill (1889) [A Fr translation can be found in MP 6, 47–48 (1893)]

Picric Powder. See under Abel Powder in Vol 1, A1-R.

Picrinita. A Spanish name for Picric Acid

Picrolonie Acid [1-(4-Nitro-phenyl)-4-nitro-3-methyl-Pyrazolone-(5)].

\[ O_2N.HC——C \_3CH_3 \]

\[ OC.N(C_6H_4NO_2).N \]

mw 264.245; N 21.21%, OB to CO_2 –115.04%; yel nds; mp 118–19°. Sol in ethanol, w, methanol, eth and Na alcoholate. Prepn is by reacting 1-phenyl-3-methyl-pyrazolone-(5) with nitric acid (d 1.49g/cc) at 10–15°. Co-reaction prods are dissoc at 60° with 33% acetic acid. The compd deton when heated quickly to 124°

Ref: Beil 24, 51 & (218)

Picronitronaphthalene. See under Trinitronaphthalene in Vol 8, N12-R to N14-R

Picryl Compounds

The picryls are usually prepd by reacting a picryl such as picryl chloride with an organic compd. Picryl peroxides and salts also exist. The entries below are picryl compds which can be considered exps, some of these such as Picryl Fluoride and Picrylpicryl Chloride have been used as exps.
Picrylacetate. \( \text{C}_8\text{H}_4\text{O}_4\text{C}_6\text{H}_2\cdot\text{O} \cdot\text{C}(\text{O}) \cdot\text{CH}_3 \); mw 271.20; N 15.50%; colorless cryst, mp 75–76°C. Prepns by heating PA with acetic anhydride.

Ref: Beil 6, 291 & (141)

There are several expls derivs of this compd; viz.,

Pyrazolidinetheneprylacetate.

\( \text{C}_4\text{H}_1\text{H}_3\text{O}_3 \); mw 313.29; N 13.42%; OB to CO\(_2\) 299.30%; pale yel crist; mp 144°C (decompn). Puffs off on heating or on contact with concd sulfuric acid

Ref: Beil 6, (141)

Trimethyleneprylacetate. \( \text{C}_1\text{H}_1\text{N}_3\text{O}_3 \); ndls; mp 140–41°C. Puffs off on heating or on contact with concd sulfuric acid

Ref: Beil 6, (141)

Picryl Ally Ether. See Allyl Picrate in Vol. 1, A139-R

Picrylaniline. See 2,4,6-Trinitrodiphenylamine in Vol 5, D1433-L. This compd forms salts, some of which are expl, viz.,

Potassium salt.

\( \text{C}_2\text{H}_9\text{O}_6\text{N}_4 +\text{C}_2\text{H}_5 \cdot \text{OK} \); mw 388.435; N 14.43%; OB to CO\(_2\) 117.39%; brn-blk crys; mp 115°C (decompn). Prepns by reacting K hydroxide in ethanol with picrylaniline (Ref 4). The compd expls on heating above its mp

Potassium salt.

\( \text{C}_2\text{H}_9\text{O}_6\text{N}_4 +\text{CH}_3\cdot\text{OK} \); mw 374.405; N 14.97%; OB to CO\(_2\) 104.70%; brn-blk crys. Sol in warm acet., ethanol and methanol. Prepns by reacting a methanol soln of K hydroxide with a benz soln of picrylaniline (Refs 3 & 4). The compd is stable in dry storage. It expls when heated.

The nitrate compds of picrylaniline are listed in Vol 5, D1434


Picryl Azide. See 2,4,6-Trinitrophenyl Azide in Vol 1, A643-L and Vol 2, B43-L

Addnl Refs: 1) Urbanski 1 (1964), 602 2) Ibid 3 (1967), 192

Picryl Chloride. See 2,4,6-Trinitrochlorobenzene in Vol 3, C250-L to C251-R

Addnl Refs: 1) Blatt, ORSD 2014 (1944), 186 2) Urbanski 1 (1964), 178, 400, 459, 460 & 461

Picryldiazide. See 1,3-Diazido-2,4,6-trinitrobenzene in Vol 2, B43-L

Picryl Fluoride. See Fluoro-2,4,6-Trinitrobenzene in Vol 6, F137-L. This compd has been evaluated at PicArn as an expl. The parameters are presented in the following limited distribution Refs: 1) H.J. Jackson et al., "A Comparative Evaluation of Selected Fluorooexplosives", PATR 3941 (1970) 2) L. Avrami et al., "Effects of Gamma Radiation on Selected Fluorooexplosives", PATR 3942 (1970) also, Addnl Refs: 1) Blatt, ORSD 1085 (1942), 77 2) Ibid, ORSD 2014 (1944)

Picryl Hydrazine. See under 2,4,6-Trinitrophenylhydrazine in Vol 7, H207-R

Picryl Hydroxylamine Toluene. See under 2,4,6-Trinitro-3-hydroxylaminotoluene in Vol 7, H247-R

Picrylhydroperoxide; Sodium Salt.

\( \text{C}_4\text{H}_2\text{O}_4\text{C}_6\text{H}_2\cdot\text{O} \cdot\text{Na} \); mw 267.14; N 15.73%; OB to CO\(_2\) 299.30%; red-blk crys; mp 154°C. Sol in ethyl acetate and w. Prepns by reacting equimolar amts of picryl chloride and Na peroxide in w. The compd is stable in dry storage. It expls when heated.

Refs: 1) Beil 6, 291 2) H. Voswinkel, German 96855 (1898)

Picrylnitramine (2,4,6-Trinitrophenynitramine).

\( \text{C}_4\text{H}_2\text{O}_4\text{C}_6\text{H}_2\cdot\text{N} \cdot\text{H} \cdot\text{NO}_3 \); mw 273.18; N 25.64%; OB to CO\(_2\) 32.21%; yel ndls or crys; mp 75–90°C (degr). Sol in ethyl acetate and w. Prepns by reacting a solution of 2-nitroanilide or 4-nitroanilide in sulfuric acid with a solution of K nitrate
in sulfuric acid at 5°. The compd is v expl and sens. Lead block expansion is 140% of PA
Refs: 1) Bell 16, 668 2) Blatt, OSRD 2014 (1944)

Picrylomamide (Oxalic acid amide-[2,4,6-Trinitroanilide]). \((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{N(H)CO.CO.NH}_2\); mw 299.22; N 23.41%; OB to CO\(_2\) -56.15%; ndles; mp 255-60° (decomp). Sol in ethanol and hot ac et.
Prepn is by heating 1 part of 2,4,6-2',4',6'-hexanitroaniline with 1p of K acid carbonate and 30p of w
Ref: Beil 12, 767

Picrylphenylenediamines. See under Trinitroaminodiphenylamines in Vol 1, A197-L & R.

Picrylpicyl Compounds. These are listed as dipicrils in Vol 5, D1488-R to D1490-L. This listing includes: Dipicrylamine, Dipicrylamino-anthraquinone, Dipicrylaminoethyl Nitrate, Dipicrylariginine, Dipicrylarboxamideacetylethane, Dipicryldianthranilide, Dipicryldisulfide, Dipicrylethane, Dipicrylithanol, Dipicrylether, N,N'-Dipicrylthiolenenediamine, N,N'-Dipicryl-ethylene-dinitramine, Dipicrylglycerylether Nitrate, Dipicrylguanidine, Dipicrylmethane, Dipicrylmethylamine, Dipicrylmethyldiethylene glycol, Dipicryloxamide, Dipicrylphenylenediamine, Dipicrylpiperazine, Dipicrylpropylene-
diamine, Dipicrylselenide, Dipicrylsulfide, Dipicrylsulfone, Dipicrylthiol-ethylbenzene, Dipicrylthio-xylene, Dipicryltolylpropyrene and Dipicrylurea. In addition, there are several other dipicryl compds of interest. They are entered next under the picrylpicyl nomenclature.

m-Picrylpicyl Chloride (3-Chloro-2,2',4,4',6,6'-Hexanitrobenzhydronitrophenyl, PIPIC).
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{H.C}_6\text{H}_2\text{(NO}_{2}\text{)\_3});\) mw 458.72; N 18.32%; OB to CO\(_2\) -47.09%; pale yel cryst; mp 186-88°. Sol in acet. Prepn is by a two step proc with the first step being the addn of pyridine to 3-methoxy-2,2',4,4',6,6'-hexanitro-
biphenyl. This is accomplished by refluxing 75ml of pyridine with 0.33 mole of the bi-
phenyl suspended in 1.2l of benz for 1 hr at 100°. The second step is accomplished by dissolving the prod of step one into 400ml of P oxychloride and warming for one hr at 100°. Ice w pptn of the second step prod is followed by filtr, w washing, drying, purification and recryst from n-hexane. A yield of 89% is obtd. Currently, the compd is used as an exp
Ref: J.C. Dacons & M.J. Kamlet, "A New Synthesis For 3-Chloro-2,2',4,4',6,6'-Hexanitro-
biphenyl, PIPIC", NOLTR 65-215 (1966)

N,N'-Dinitro-N,N'-Picrylpicyl-Propyl-1,3-Di-
amine. \((\text{O}_2\text{N})_3\text{N}(\text{CH}_2)_2\text{N(NO}_{2}\text{);}\)
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{C}_6\text{H}_2\text{(NO}_{2}\text{)\_3};\) mw 587.33; N 24.01%; OB to CO\(_2\) -51.76%; yel cryst; mp 202°. Prepn is by reacting nitric acid with N,N'-diphenylpropylene-1,3-diamine. The compd is expl
Ref: Beil 12, {1741}

1-Picryl-Semicarbazide (1-[2,4,6-Trinitrophenyl]-Semicarbazide).
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{NH.NH.CO.NH}_2\); mw 286.23; N 29.37%; OB to CO\(_2\) -55.90%; yel ndles; mp 218-19° (decomp). Sol in alc q solvent; sl sol in solvents such as acet and acet ac. Prepn is by reacting picryl chloride and semicarbazine inaq ethanol.
Ref: Beil 15, [222]

1-Picryl Semioxamazine (1-[2,4,6-Trinitro-
phenyl]-semioxamazine).
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{NH.NH.CO.CO.NH}_3\); mw 313.25; N 26.84%; OB to CO\(_2\) -56.19%; mp 249-50° (decomp). Sol in alc alkalies; sl sol in organic solvents. Prepn is by reacting picryl chloride with semioxamazine in boiling ethanol.
Ref: Beil 15, [222]

1-Picryl-Thiosemicarbazone (1-[2,4,6-Trinitro-
phenyl]-thiosemicarbazide).
\((\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{NH.NH.CS.NH}_2\) (becomes the destmotic form); mw 302.28; N 27.81%; OB to CO\(_2\) -58.22%; bright yel ndles; mp 183-34° (decomp). V sol in ethanol, acet and acet ac; sl sol in benz, chif and petr eth. Prepn is by re-
acting picryl chloride with thiosemicarbamide in ethanol at 100°C
Ref: Beil 15, [222]

Picryl Sulfide. See Hexanitrodiphenylsulfide in Vol 5, D1477-R

Picryl Sulfone. See Hexanitrodiphenylsulfone in Vol 5, D1480-L

Picryl tetrazoylamine.
\[ \text{NHNH} \]
\[ \text{C}_6\text{H}_2(\text{NO}_2)_3 \]
\[ \text{N} \]
mmw 293.22; N 38.22%; OB to CO\(_2\) −54.57%;
prepn is by reacting picryl chloride with tetrazo-
lylamine. The compd explds on impact
Ref: Blatt, OSRD 2014 (1944)

Picryl tetrazylazide. A compd patented by W. Fiedrich for use as a primary filler in de-
notors and detonating fuzes. No method of prepn or structure is revealed in the patent
Ref: W. Fiedrich, USP 2170943 (1939) & CA, not found

1,10-Dinitro-1,4,7,10-Tetra-Picryltriethylene-
tetramine (N,N'-Bis-[2-(2,4,6-N-Tetranitro-anilla-ino)-ethyl]-N,N'-dipicryl-ethylenediamine).
\[(\text{O}_2\text{N})_2(\text{C}_6\text{H}_2)_2\text{N}_2\text{CH}_2\text{CH}_2\text{N}_2\text{CH}_2\text{CH}_2\cdot \text{NO}_2 \]
\[(\text{O}_2\text{N})_2(\text{C}_6\text{H}_2)_2 \]
mmw 1080.82; N 23.33%; OB to CO\(_2\) −62.18%;
bright yel cryst; mp 165°C (decompn). Prepn
is by reacting nitric acid with 1,4,7,10-tetra-
kis-(2,4-dinitro-phenyl)-trithylenetetramine at
−15°C. When quickly heated the compd explds
Ref: Beil 12, [1740]

Picrylurea (2,4,6-Trinitrophenylurea).
\[(\text{O}_2\text{N})_2(\text{C}_6\text{H}_2)_2\cdot \text{N}((\text{H})\text{CO})\text{NH}_2 \]
mmw 271.21; N 25.83%; OB to CO\(_2\) −56.05%; yel cryst; mp
201−03°C (decompn). V sol in ethanol, eth,
acet and acet ac; sl sol in chl and petr eth.
Prepn is by reacting an alc soln of ammonia
with N-nitro-N-ethyl-N'-[2,4,6-trinitro-phenyl]-
urea
Ref: 1) Beil 12, [423] 2) M. Giua, Gazz
55, 665 (1925) & CA 20, 1061 (1926)
3) E.C.A. Kniphorst, Rec 44, 701 (1925) & CA
20, 589 (1926)

Piper Explosives. Safety expls patented in
1893–94 in Fr. A blend of aromatic nitro-
compds with AN, using a solvent common to
both ingredients. The incorporation of a small
amt of alc in some expls was recommended.
One of these expls was "Ronsalite" (qv)
Ref: Daniel (1902), 631

Pierre and Potgiisser Explosive. A safety expl
patented in 1896 contg AN 93, Nitroaniline 5,
and Mn dioxide, Pb dioxide or Cr trioxide 2%
Ref: Daniel (1902), 631

Pierrit. See Vol 3, C443-R

Piezoelectric Gages. See under Closed Bomb
(or Vessel) Techniques in Vol 3, C339-L to C345

P.I.G. and P.S.G. Brit designations for Percent-
age Initiation by Grit and Percentage Sensitiza-
tion by Grit
Particles of grit such as carbonabund, when
added to an expl, can artificially create "hot
spots" (see Vol 7 H170-L to H175-R) when
the expl is suddenly compressed by impact as
in an impact sensy device. Only grit particles
of mp higher than that of the expl can initiate
temp hot spots and thus increase the sensitivity
of the expl
The values for both P.I.G. and P.S.G. are
computed from the areas under curves generated,
using impact sensy devices, by plotting the num-
ber of impacts leading to expl detonation vs
impact height. The two terms differ only in the
manner of defining detonation. For P.I.G.,
the area under the curve is based on complete
detonation or failure, a partial expln being called
Table 1
Relative Sensitivity Based on Figure of Insensitivity (F.I.) (from Ref 3)

<table>
<thead>
<tr>
<th>Explosive</th>
<th>F.I. of Pure Explosive</th>
<th>Number of Grit Particles/Cap</th>
<th>P.I.G. or % Initiation Sensitization</th>
<th>P.S.G. or % Gas Sensitization</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>120</td>
<td>60</td>
<td>69</td>
<td>60</td>
</tr>
<tr>
<td>RDX/Wax</td>
<td>100</td>
<td>60</td>
<td>57</td>
<td>-</td>
</tr>
<tr>
<td>PA</td>
<td>100</td>
<td>60</td>
<td>67</td>
<td>-</td>
</tr>
<tr>
<td>RDX</td>
<td>64</td>
<td>60</td>
<td>61</td>
<td>68</td>
</tr>
<tr>
<td>PETN</td>
<td>38</td>
<td>60</td>
<td>68</td>
<td>68</td>
</tr>
<tr>
<td>Tetrayl</td>
<td>72</td>
<td>12</td>
<td>48</td>
<td>23</td>
</tr>
<tr>
<td>RDX</td>
<td>64</td>
<td>12</td>
<td>52</td>
<td>49</td>
</tr>
<tr>
<td>PETN</td>
<td>38</td>
<td>12</td>
<td>66</td>
<td>64</td>
</tr>
</tbody>
</table>

a failure. For P.S.G., the area under the curve is based on gas evolution, each sample cap giving a quantity of gas greater than exptl error being called an ignition whether detonation occurred or not. Thus to express either term mathematically:

P.I.G. or P.S.G. =

\[ 100 \times \left( 1 - \frac{\text{Area under expl with grid curve}}{\text{Area under pure expl curve}} \right) \]

Table 1 illustrates the difference in values obtained using three impact sensy techniques, F.I. (see Vol 6, F39-R to F40-R), P.I.G. and P.S.G. The expls used contain known percentages of -100 to +200 mesh carbonunof of 1.2 x 10^-2 mm^2 avg particle cross section


**Pikrinäura.** Ger for Picric Acid

**Pikrit.** See under Picrit in this Vol

**Pile Driving Device.** Said to have originated in America, this device uses a cartridge of expl placed between the head of a wooden pile and a driving ram. The expln of the charge drives the pile into the ground and simultaneously raises the ram which, upon falling, drives the pile further. This idea was utilized in “drop hammers” which were explosively, not steam, operated

Ref: Daniel (1902), 631

**Pile Test for Dynamites** (Épreuve de Pieux ou de Pilotis). In order to determine the impulsive energy or work (in kg/m) performed by various Dynamites, Col Prodonovic (Hungary) proposed the following test in 1881:

A charge (one or several) of the expl to be tested is attached to an iron disk 38cm in diam and 11cm thick, and covered either with sand or clay. The disk is placed on the top (head) of a wooden pile inserted in the ground. Alongside of this pile is placed a similar pile with a charge of a “standard” expl. After exploding both charges simultaneously, the depth of penetration of the piles into the ground is measured and compared

Ref: Daniel (1902), 633

**Pigou Propellants.** Smokeless proplnts, patented in 1896, manufd by blending nitrated hydrocellulose with Ba nitrate and starch

Ref: Daniel (1902), 632

**Pike and Thew Explosives.** Patented in Engl in 1897; prepd by mixing nitrated potato wastes with other ingredients

Ref: Daniel (1902), 632

**Pikratol.** Ger for Ag Picrate. See in this Vol under Picrates, Inorganic
Piling and Stacking of Ammunition. Techniques using geometry and/or physical protection have been evolved for ammo which reduces its vulnerability during temporary combat area storage (Ref 3), increases its safety in transport, and increases its shelf life while in permanent storage. Descriptions and drawings of the arrays of all types of end-items on individual pallets, in individual packages, as well as the quantity-distance relationships for safety in piling and stacking these items are shown in Refs 1 and 2. See also under Packaging and Packing of Ammunition in this Vol.

Refs: 1) Anon, “Storage and Outloading Primary Index”, TM 743-200-1 (July 1970)
3) H.J. Reeves, “General Principles of Vulnerability Reduction of Stacked Ammunition”,
BRL MR No 2376 (1974)

Pimelic Acid and Derivatives.

Pimelic Acid (Heptanedioic Acid or 1,5-Pentanedicarboxylic Acid). HOOC·(CH$_2$)$_2$·COOH; mw 160.17; white prisms; mp 106$^\circ$; bp 272$^\circ$ at 100mm (subl), and 212$^\circ$ at 10mm; d 1.329 g/cc at 15$^\circ$. Sol in w, ethanol, eth and hot benz. Prepn is by oxida of cycloheptanone, capric acid or oleic acid; treatment of salicyl acid with Na in amyl alc, or by decarboxylating 1,1,5,5-pentanetetraacarboxylic acid with heat

Pimelic acid has been combined with cis and trans-1,4-cyclohexanediol to give polyesters, and with m-xylene-α,α'-diamine or polyethylene-1,5-diamine carboxylic acid with heat.

The acid is used as the parent compd to form the excls presented below


4,4-Dinitroheptanediol Azide.

N$_3$OC·CH$_2$·CH$_2$·CO(NO$_2$)$_2$·CH$_2$·CH$_2$·CON$_3$; mw 300.26; N 37.33%; OB to CO$_2$ -63.94%; colorless crysts, mp 68-69$^\circ$ (decomp). Sol in chlf.

Prepn by dropwise addition at 5-10$^\circ$ of a 0.035 mole soln of 4,4-dinitroheptanediol chloride in ace to a 0.14 mole soln of Na azide in w. Wpptn and washing gives a 90-95% yield

Refs: 1) Beil, not found 2) L. Herzog et al, JACS 73, 749-51 (1951) & CA 45, 5609 (1951)

4,4-Dinitropimelic Acid (DNPA,4,4-Dinitro-1,7-Heptanedioic Acid).

HOOC·(CH$_2$)$_2$·C(NO$_2$)$_2$·(CH$_2$)$_2$·COOH; mw 250.23; N 11.19%; OB to CO$_2$ -70.34%; white cryst plates; mp 137$^\circ$; d 1.52g/cc. V sol in ace; sol in w and v sol in toluene. Prepn is in two steps; the first being the synthesis of the di-methyl ester of 4,4-dinitropimelic acid followed by acid hydrolysis to yield the acid. In the first step 13.5 moles of methyl acrylate is added dropwise with stirring at RT to anaq soln of 2.5 moles of K dinitroethanol. The addn is completed in three hrs with eight more hrs of stirring requ to complete the reaction. After completion of the stirring, the ester is extrd with eth decolorized with charcoal, and the eth removed under vac. The impure ester is then recryst from methanol. The mp of the 58% yield is 45$^\circ$ (Ref 4). The second step hydrolyzes 0.14 mole of the ester by refluxing it with 350ml of 18% hydrochloric acid for several hrs. After cooling, the 4,4-dinitropimelic acid is crystd from w. This step has a yield of 95-97%. The total yield based on K dinitroethanol is 55 to 56% (Refs 3 & 5). Several pilot plant and comml processes are given in Refs 6 & 7

4,4-Dinitropimelic acid is compatible with NC in a 20% mixt of the acid; Qc, at 25$^\circ$ of 3010cal/g (liq w ref); Qc of -235kg cal at 25$^\circ$ and 1 atm press; has an impact sensy of >100cm using a BM app with a 2kg wt; a thermal stability at 65.5$^\circ$ of over 5 hrs; a thermal stability at 134.5$^\circ$ of over 40 mins (unchanged after 5 hrs); and is stable in storage at RT (Ref 3).

The acid is used as an intermediate in the synthesis of polyvinylaliphatic expts and proplts, and as a monomer in a propyl polymer developed by the Aerojet Engg Corp which is presented next


**The Polyester Polymer 4,4-Dinitro-pimaly Chloride and 2,2-Dinitro-1,3-Propanediol.**

\[ \begin{align*}
&\text{Q} \quad \text{C}(\text{CH}_2)_2\text{C(NO}_2)_2\text{CH}_2\text{C.O.CH}_2. \\
&\text{C(NO}_2)_2\text{CH}_2\text{O)}_n
\end{align*} \]

mw (380.32)\text{H}, approx 4000--9000; N 14.73%; OB to CO\text{2} 58.90%; amber molded pellet or cream colored powder; softening pt 170--185\text{°C}.

Sil sol in acet, dioxane and tetrahydrofuran; v sol in dimethylformamide. Prepn is a two-step process which first involves the synthesis of the chloride, and then the polyester. The chloride is prepd by cautiously heating a mixt of 0.2 mole of 4,4-dinitropimelic acid with 90cc of thionyl chloride at reflux for 2 hrs. Hot filtrn is followed by rapid cooling to --15\text{°C}. Recryst from thionyl chloride gives a 95% yield of the chloride with a mp of 57\text{°C} (Ref 4). The polymer is then prepd using equiv amts (0.1 mole) of the monomers which are mixed with 50ml of dioxane under dry nitrogen at 100\text{°C} for 173 hrs. The washed polymer is then vac steam distd at 25\text{°C}, and dried over phosphorous pentoxide at 2mm (Ref 3).

The polyester has a Qc of 3020kcal/g; a 50% pt impact sensy of 85--95cm with a BM app with a 2kg wt; a specific impulse of 204lbf-sec/lb; a thermal stability of 215 mins at 65.5\text{°C} and 15 mins (unchanged appearance of the sample after 5 hrs) at 134.5\text{°C} (Refs 2 & 3).


Pin-Fire Cartridge System. A cartridge ignition system invented in 1836 by LeFaucheux of Paris. It was the first practical cartridge system which contained in one unit the cartridge case, the propint, the bullet and the primer cap. A version of this invention is still used today in blank pistols designed in Europe. The cap was placed inside the cartridge near the base in such a manner that the priming compd, usually Fulminate of Mercury, faced the pin which was parallel to the base and protruded thru the side of the cartridge. When the protruded end of the pin was struck by the gun's hammer coming down vertically on the side of the cartridge (instead of penetrating horizontally from the rear, as is done in modern cartridges), the other sharpened end of the pin struck the primer and caused the ignition of the primary compn and of the propint.


Pinite and Derivatives. See Inositol and Derivatives in Vol 7, 1109-L to 1110-R

Pin Method or Pin-Oscillograph Method For Detonation Rate Measurement. See Vol 3, C315-R

Pin Switch Technique for Measuring Detonation Velocity. See Vol 3, C313-R to C319-L

"Pinwheel". A rocket helicopter developed in 1951 by Rotor-Craft Corp of Glendale, Calif.
It weighs 100 lbs and is designed to carry one person. Thrust is generated by self-starting, throttle controlled liq fuel rockets mounted in the tips of the two small rotor blades. The rotor is attached to a steel tube which curves downward to support the fuel tanks, a pilot seat and a cargo hook. A tube extending backward from the rotor hub carries a small rudder, and another extending forward and down is the pilot's control column.

Ref: Anon, Ordn 36, No 190, 618 (1952)

Piobert's Law of Combustion. When a solid grain of a propelt (such as smokeless powder) is ignited in air, each surface burns independently and progressively in parallel layers and at the same rate. Indeed, the process of burning is so regular that if it is stopped before completion, the unburned portion of the grain will have the same shape as the original grain, but it will be smaller in size.

The same regularity of burning is observed in grains with perforations, except that the shape of the partially burned grains is not exactly the same as the original grains because the diameter of the outer layer diminishes and the diameter of the inner layer increases during burning.

That the burning proceeds uniformly by layers may be shown by firing a gelatinized NC powder from a gun too short to allow total consumption of the proplnt. The grains ejected from the nozzle will be identical in geometry but differ in size from the original grains.

It should be noted that Piobert's Law is valid only for non-porous powders which deflagrate but do not expel. Hence, it is inapplicable to powders which are porous such as BlkPdr, non-gelatinized, compressed NC, etc. See " Burning and Burning Characteristics of Propellants for Artillery Weapons and Small Arms" in Vol 2, B346-L to B347-L.

Refs: 1) Marshall 1 (1917), 310–11
2) Pérez Ara (1945), 417–18
3) S. Fordham, "High Explosives and Propellants", Pergamon Press, NY (1966), 194

PIPE. A plastic expl developed by the US Ordn Corps during WWII. It is a mechanical mixt of PETN (81%) and Gulf Crown E Oil (19%); mw 300; N 18.08%; OB to CO₂ -74%; d 1.35 g/cc (hand tamped). PIPE has a detonation rate in a hand tamed 1.0-inch diam charge (1.37 g/cc d) of 7075m/sec; a fragmentation test using a 3-inch HE, M42A1 proj of 428 frags (514 for TNT); a friction pendulum test of "unaffected" with both steel and fiber shoes; a heat test at 100°C of 0.17% loss in 48 hrs, an addnl 48 hrs showed no loss and no expl in 100 hrs; a hygroscopic gain of 0.02% at 90% RH and 30°C; an impact sensy of 11 inches (8 inches for RDX) using a 27mg sample in a PicArsn app with a 2kg wt; a rifle bullet impact test of "100% unaffected"; a sensy to initiation of 0.20g with either Mercury Fulminate or Pb Azide; and a vac stab test at 100°C, using 5g sample, of 0.48sec in 40 hrs, and over 11cc in 16 hrs at 120°C. It is considered a Class 9 exp of Group I compatibility and is stored dry. PIPE is used as a demolition expl.


Pipeline Digester for Nitrocellulose. Known as the Milliken continuous digester. It consists of approx 0.8 mile of 4-inch diam chrome steel tubing in numerous sections connected by numerous return bends. According to Yeager:

"The first sections are steam jacketed, the intermediate sections simply insulated to hold the temperatures reached by the mass in the heated part, and the final section is provided with a cold water jacket to stop the digestion and cool the mass below the atmospheric boiling point of water. Since the digestion must be conducted under pressure to permit the necessary temperature, the required hydrostatic head on the entire system is provided by piping the mass from the discharge of the digester up over a 200-ft tower, then down again to a final treatment and sampling tub. The tower was chosen as the best method of supplying back pressure, since other methods such as valves and pumps would be unreliable due to fouling.

Nitrocellulose is always in motion in the digester and well suspended in water, so that each fiber receives uniform treatment, producing a uniform viscosity much superior to the batch product. The continuous product has no oppor-
tunity to pick up contamination from brick and cement and the process eliminates gas pockets where overheating and possible explosion could occur. Labor required is less and much disagreeable work is eliminated. Furthermore, control is superior..."


Piperazine and Derivatives. See Diethylene-diamine and Derivatives in Vol 5, D1230-R to D1231-R. An addn ref is: A.T. Blomquist, OSRD 4134 (1944), 7 & 68


Piperidine and Derivatives

Piperidine (Hexahydropyridine or Pentamethyl-enameine).

\[
\text{NH; mw 85.15; N 16.45%; colorless liq; mp } -9{}^\circ; \text{ bp 106}{}^\circ; \text{ d 0.8606g/cc at 20/4}{}^\circ; \text{ RI 1.4530. V sol in ethanol and w; sol in eth., acet., benz and chlf. Prepn is by reducing py with Zn and HCl or by heating } \varepsilon\text{-iodo-}n\text{-aryl-}
\]

amine with w. Piperidine has a fl pt in air of 3{}^\circ. It is the parent compd for organometallic azides used in heat resistant plastics; compds used as anti-materials, insect repellants, anti-radioactivity agents, psychotropic drugs and chemical warfare agents; also to the expls presented below


1,3,3,5,5-Pentanitropiperidine.

\[
\begin{array}{c}
\text{(O}_2\text{N)}_2 \\
\text{N NO}_2
\end{array}
\]

\[
\text{(O}_2\text{N)}_2 \\
\text{N NO}_2
\]

mw 296.21; N 23.65%; OB to CO\textsubscript{2} -70.22%; cryst; mp 120-25{}^\circ; d 1.82g/cc. Sol in chlf.

Prepn is by treating 0.4g of 3,3,3,3,3-Tetranitropiperidine with a mixt of 8ml of 100% nitric acid and 8ml of acetic anhydride at 5{}^\circ. Yield is 78%. Pentanitropiperidine is a brisk expl with a Q\textsubscript{C} of 2056cal/g

Refs: 1) Beil, not found 2) M.B. Frankel, USP 2978452 (1961) & CA 55, 17657 (1961); Ibid, Explosivst 1, 243 (1964)

There are four piperidine expl addn compds extant, viz,

Piperidine-Chronic Acid.

(C\textsubscript{6}H\textsubscript{11}N)[HCrO\textsubscript{4}]; mw 218.20; N 6.42%; OB to CO\textsubscript{2} -80.66%; cryst; mp, expls when heated; v sol in w.

Ref: Beil 20, 12

N-Perchlorylpiperidine.

\[
\begin{array}{c}
\text{NClO}_3 \\
\text{NClO}_3
\end{array}
\]

OB to CO\textsubscript{2} -114.56%; mp, expls violently on heating; RI 1.4646. Sol in w and eth. Prepn is by reacting an aq soln of piperidine (8.0g/250ml w) with perchloryl fluoride gas at RT. The gas is bubbled thru the soln for 20 mins at a rate of 170cc/min. The soln is then nitrogen purged for 10 mins, extrd with eth, dil HCl washed, and dried at RT under vac. Yield is 66%. The perchlorate is a dangerously sensitive mat. It expls on heating, exposure to sunlight or on contact with anhyd piperidine. It is de-sensitized by adsorption on powd alumina and
can be stored indefinitely at $-80^\circ$.

**Piperidine Triazido Cuprate.** [Cu(N$_3$)$_3$](C$_6$H$_7$N); mw 274.81; N 50.98%; OB to CO$_2$ –90.25%; dark red-brown crystals; mp 178–80°C (explosive). Sol in w. Prep is by dissolving Cu azide in piperidine. A brisant expl, but rather insensitive to shock, having an impact sensy of 100cm using a 2kg drop hammer.
Refs: 1) Bie, not found 2) A. Cirulis & M. Straumanis, Ber 76B, 825–30 (1943) & CA 38, 1970–71 (1944)

**Diperidino-Tetrazido Cuprate.** See Vol 5, D1490-L

**Pipitz Propellant.** Patented in 1899, consisting of grains prep by coating a core of NC with collodion. An overcoat of paraffin was applied after solvent evap.
Ref: Daniel (1902), 633

**Piquet and Pochez Explosives.** Expls prod in a patented procedure by nitration of manure.
Ref: Daniel (1902), 633

**Pirodialiti.** See Pyrodialites in Vol 6, E366-R to E367-R

**Pirokollodion (Pyrocollodion).** A single-base proplnt contg NC of 12.45% N invented by D.I. Mendeleev in 1891. This proplnt served as a prototype for the Pyrocellulose single-base proplnt introd in the US in 1895 by Bernadou and adopted by the Navy. Pyrocellulose, or simply “Pyro” is based on NC of about 12.6% N. See “Collodion Cotton or Pyroxylin” and “Pyrocellulose, Pyro or Pyrocotton” in Vol 2, C103-R to C106-L.

**Pironome.** See “Pyronome (1881)” in Vol 2, C206-L

**Pirsch Propellant.** Patented in 1897; prep by mixing an acetonic soln of NC with 10–15% Dinitrobenzene, grinding and evap the solvent.
Ref: Daniel (1902), 633

**Pitite.** An expl manufd in Engl in 1898 by the New Explosives Co., Ltd. It contained NG 25–27, K nitrate 30–35, Ba nitrate 30–35, wood flour (contg 5–15% moisture) 40–43, sulfated benz 0.5, Na carbonate 0.5, and Ca carbonate 0.5 parts.
Ref: Daniel (1902), 634

**Pitite No 2.** A British “permitted” expl consisting of NG 24, wood meal 34.5, K nitrate 29.5, amm oxalate 8, and w 3.5%.
Refs: 1) Daniel (1902), 633 2) Barnett (1919), 135

**Pittius Explosives.** C. vanPittius of Holland obtd a BritP in 1910 on expls consisting of combustible mats and oxidizers. The combustible constituent is prep by mixing resin (10p) and stearin (5p) together at 150°, and incorporating paraffin (10p) and a blend consisting of TNT (25p) and NG (5p) or NC (3p). Molten TNT (50p) is then added and blended while maint the mixt at 85°. The reddish-brown mixt is termed “TNT paste”. To use this expl the TNT paste is mixed with oxidizers, viz,
- a) TNT paste 20, K nitrate 30, amm perchlorate 30 and K perchlorate 20%; b) TNT paste 8 and amm nitrate 92%
Ref: Colver (1918), 679–80

“Planeatita”. Expls having a greater energy, velocity of deton and brisance compared to that of Dynamites; viz,
- a) TNT 10 and liq nitrogen peroxide 12p;
- b) MNT 30.3 and liq nitrogen peroxide 69.7%. These mixts are less dangerous to handle than “Panclastites” (qv).

Plane Detonation Waves with Finite Reactions. See “Detonation Waves: Steady-state, One-Dimensional Reaction Waves with Finite Reaction Rate” in Vol 4, D703-R to D704-R.

Plant Layout, Location, Design and Construction. For information on the special techniques required in the loading and fabrication of exps pertinent to amm plant layout and design, see the entry under that title in Vol 7, L46-L to L57-L. For what has been done to accomplish modernization of munitions plants now extant, see “Modernization Engineering Project for US Army Ammunition Plants” in this Vol, M147-L to M148-R. The problem of pollution created by amm plants is examined in an article under this topic in this Vol.

The following ref is of general interest to this topic: Kirk & Othmer, 2nd Ed, 15 (1968), 689–99: M.M. Goetz, “Plant Layout”, 700–20: L.V. Kaltenbrucke, “Plant Location”.


Plasma; Its Definition, Generation and Ordnance Applications. The term plasma is defined by Funk & Wagner (Ref 44a) as “... any gas composed of... equal numbers of positive ions and electrons...”. This definition has been expanded enormously in terms of concept, theory
and mathematical presentation, as can be seen by the extensive list of refs on these subjects; viz, refs 2 thru 16, 26 thru 28, 30, 33, 34, 36 thru 39, 42, 45, 46 & 48.

Plasma can be generated in many ways; viz, by detonation (see "Detonation Plasma" in Vol 4, D258-L to D264-L, D348 & D471-R to D474-R); by controlled nuclear fusion, the abundant energy source of the future (Refs 3, 9 & 12); by uncontrolled nuclear fission and fusion as in atomic and fusion expls (see "Atomic (or Nuclear) Bomb" and "Atomic (or Nuclear) Energy; Atomic (or Nuclear) Reactions; Atomic (or Nuclear) Explosions" in Vol 1, A499-L to A504-L); by the combustion of a propnt, liq or solid, as in a gun, internal combustion motor or rocket engine (see under the appropriate titles in the Encycl); or by the combustion of any fuel leading to an ionized gaseous state.

The ordnance applications of plasma are numerous; including not only the above referred means of generation for constructive purposes, destructive purposes, motive power, etc; but, also for such purposes as studying the effect of expl detonation on plasmas and vice versa (Refs 17, 18, 35, 44, A O and W*); the use of plasma jets as research, manufac and testing tools (Refs 2, L, P & S); the use of plasma as light sources (Ref R); studying the effect of interstellar plasma on RF signals (Refs O and V); studying the energy source plasma obtained using nuclear fuel (Ref X); studying the parameters of plasma physics (Refs 19, B, C, E, G, J and K); plasma pulse power electricity generation (Ref F); the measurement of plasma flow (Ref 20); the use of plasmas for rocket propulsion (Refs 22, 23, 25, 40, 47, T and V); the generation of electricity from plasma using pyrots (Ref D); the simulation of rocket plumes using pyrot generated plasma (Ref M); the study of shock generated plasma on re-entry vehicles (Refs 41 and H); and the study of techniques such as spectroscopy to measure parameters such as plasma temp (Refs 29, 32 and N).

that may arise in the application of polymers. Although not as extensive as the expI.
compatibility data, it represents another unique contribu-
tion in information retrieval

From time to time PLASTEC specialists publish technical reports and notes on information
to be of interest to the technical community. These reports are sold by NTIS, located
at 5285 Port Royal Road, Springfield, Virginia
22161 at a price commensurate with their
handling and printing cost. A selected list of
PLASTEC reports and notes is given under Refs
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Glass Laminates", PLASTEC Rept 1 (1960)
2) M.E. Gigliotti, "Design Criteria for Plastic
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Levi, "Literature Survey on Thermal Degra-
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5) A.H. Landrock, "Fluidized-Bed Coating with
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the Reactions Reported in Picatinny Arsenal

Plaster Shooting. See mudcapping or Adobe shooting under Agriculture and Forestry Uses of Explosives in Vol 1, A113-R; also, under Mudcapping in Vol 8, M160-R

Plastex Eversoft. A pre-WWII Brit Dynamite contg NG + Nitroglycerol 25.5, colloidon cotton 0.5, DNT+TNT 2.5, AN 35, woodmeal 2.5, and NaCl 34%. BallPend swing 2.45” vs 3.27” for Brit Standard Gelnite contg 60% NG Ref: Marshall 3 (1932), 120

Plastic Bonded Explosives. See under PBX in this Vol

Plastics and Polymers, Compatibility with Explosives. See refs 10, 25, 32 & 33 under PLASTEC in this Vol

Plastics and Polymers, Military Applications. See refs 19 & 41 under PLASTEC in this Vol

Plastit. A WWII plastic expl contg RDX 64, colloidon cotton 3.5, and liq or semi-liq nitrohydrocarbons 32.5% (Refs 1 & 2). Ref 3 states that it is a Swiss trade name for a plastic mil expl based on PETN, manuf by Schweiz. Sprengstoffe-Fabrik A-G Refs: 1) All&EnExplos (1946), 127 2) PATR 2510 (1946), Ger 134-R 3) Private communication from Dr. A. Stettbacher (Dec 14, 1953)

Plastolit (Swiss). See Vol 3, C444-L
Plastomenites. Proprietary patented in Ger by Gütlinger in 1889–90, consisting of NC, Nitrolignine, Nitrosugar, Nitrostarch, etc., gelatinized by the addition of nitrate of aromatic compds such as benz, toluene, phenol, naphthalene, etc. Inorganic nitrates, chlorates, chromates, picrates, etc., could be added to the mix.

One of the varieties of Plastomenites used in Ger as sporting powder was prepd by melting 3% of DNB on a w bath, and adding 1% of NC.

In Engl, Plastominites consisted of NC, DNB and Ba nitrate, and three varieties were known; JCP (for sporting use), BP (for carbines), and KMP (for mil use).

Their compn was modified by Gütlinger in 1897 by incorporating 0.5 to 10% of powdered rosin (colophony). According to Colver (Ref 2), some Plastominites consisted of DNT 80 and Nitrolignin 20% (blended in a hot condition), and occasionally, some Ba nitrate. After the incorporation, the fused mass was granulated.


Plastrit or Plastrotol. Plastic expls patented in 1906 by C.E. Bichel. They were prepd by mixing 85–87% of TNT with liq and/or solid resins (such as copaiba, balsam, benzoin gum, styx, turpentine, etc.), and collodion cotton, with or without liq DNT.

Refs: 1) Colver (1918), 249 2) PATR 2610 (1958), Ger 134–35

Plastrita (Span). A soft, doughy exp tl plastic expl prepd by La Fabrica de Polvoras of Granada, Spain, by mixing pulverized TNT with collodion. It expl power was less than that of TNT.

Refs: 1) Sancho (1941), 152 2) Pérez Ara (1945), 505 3) Vivas, Feigenspan & Ladreda, 2 (1946), 380

Plate Danger Tests or Plate Tests. See Vol 1, Introduction XIX to XX

Platinum. Pt; aw 195.09; silver-gray, lustrous, malleable and ductile metal; face-centered cubic structure; also prepd in the form of a black powder (Pt black) and as spongy masses (Pt sponge); mp 1773.5°C; bp about 4530°C; d 21.447 g/cc.

Pt is attacked by bromine trifluoride at 280°C in the presence of K fluoride (Ref 5). Finely divided Pt and some other metals will cause a mix of H2 and O2 to expl by at ordinary temps (Ref 1). A little Pt black dropped into a hydrogen peroxide soln can cause an expln (Ref 2). Pt and molten Li react violently at 540°C ± 20°C (Ref 7), and an incandescent reaction occurs when it is warmed gently in gaseous oxygen difluoride (Ref 6). The decomp of 92% permonsuluric acid is expl in the presence of smooth or finely divided Pt (Ref 3). The reacting mass formed by the mix of P and Pt can become incandescent when heated (Ref 8).

Dry, unused Pt catalyst has expld while being screened (Ref 4).


Platinum Compounds. Several Pt compds, including trimethylplatinum derivatives are explosively unstable (Ref 9). Ammmipentahydroxoplatinum, H8NO3Pt, expls fairly violently above 205°C, as does the pyridine analogue (Ref 3). Ammonium Hexachloroplatinate(2)-, Cl6H8N2Pt, when boiled with alkali gives a product which, after drying, will expl violently on heating alone to 205°C or with combustible materials (Ref 5). Ammonium Tetranitratoplatinate(II), H8N4O8Pt, decmps explosively on heating (Ref 1). Cis-Diaminedinitroplatinum(II), H8N4O4Pt, decmps explosively at 200°C (Ref 11). Hexamethylplatinum, C6H18Pt2, expls sharply in a shower of sparks on heating (Ref 8). Platinum(IV) Oxide, PtO2, when added as a catalyst to a hydrogenation reaction in acet ac caused an immediate expln (Ref 4). Both Platinic Bromide (PtBr4) and Platinic Chloride (PtCl4) are vigorously attacked by bromine trifluoride (Ref 10). Plati- nous Hypophosphite, Pt(H3PO3)2, liberates spontaneously flammable phosphine above 130°C.
(Ref 6). Platinum ammine nitrates and perchlorates may be impact sensitive. Pt(NH₃)₄(NO₃) and Pt(NH₃)₄(OH)₂(NO₃)₂ detonate when heated (Ref 7). Potassium Dinitrooxalatoplatinate(2-), C₃K₂N₂O₈Pt, decomp's violently at 240°C (Ref 2). Tetramethylplatinum, C₅H₁₀Pt, expls weakly on heating (Ref 8), while Trimethylplatinum Hydroxide, C₃H₁₀OPt, detonates (Ref 12)


**Pleopentaerythritol.** A mixt of polypentaerythritols consisting of di- and tri-pentaerythritols with some tetra- and other comps, which remain after the separation of PE from mother liquor in the prep of PE by the condensation of formaldehyde and acetaldehyde in the presence of alka.

Pleopentaerythritol can be nitrated, and the resulting mixt is an expl which can be utilized in the prep of commercial expls. Nitropleopentaerythritol is not as powerful as PETN or DPEHN


**Plessit.** A Ger blasting expl introduced during WWI contg K chloride with not more than 9.5% kerosene and 0.5% albumen. One variety, Wetter-Plessit III, used in coal mines, contained NaCl as well

*Ref:* Marshall, Dict (1920), 76

**Plodex Explosives.** Patented in 1898; contained as a base products prepd by the nitration of potato and beet-root wastes.

*Ref:* Daniel (1902), 635

**Plomoplastira (Span).** An expl obtained by mixing Plastrita (qv) with Pb nitrate. It is as powerful as TNT, possesses a higher d, is less sensitive to mechanical action, and does not evolve poisonous gases on expln

*Ref:* Sancho (1941), 153

**Plosophore or Explosophore.** See under Auxo-explose or Auxophosphore in Vol 1, A513-R to A514-R

**Plugs, Closing (Closing Plugs).** These are threaded cylindrical blocks made of steel, Al or plastic material, and are provided with a head to fit a wrench. The plugs are intended to close the fuze hole of those fixed or semi-fixed shells which are shipped or stored unfuzed, although loaded with HE. Plugging of the fuze hole is necessary in order to prevent the entrance of foreign material as well as to protect the threaded portion of the hole from damage during handling of the shell

In so-called deep-cavity shells, a short length of cardboard tubing, called a spacer, is provided and placed between the supplementary charge and the closing plug in order to keep the former from movement

*Ref:* Anon, OrdTechTerm (1962), 227-L

**Plumbatols.** Buff colored expls consisting of Pb nitrate 60 or 70 and TNT 40 or 30%, which were used expdly during WWII. They could be cast loaded, and not being hygroscopic, could be stored dry. They were manufd by simple mechanical mixing of Pb nitrate in molten TNT

The 70/30 variety had the following properties: OB to CO₂ 5.4%; OB to CO +9.3%; 5 sec expln temp, 223°C; impact sensitivity, 13" vs 14" for TNT (using PicArsn app with a 2Kg wt); brisance by 200g bomb sand test, 32.4g vs 48.0g for TNT; deton velocity at d 2.89g/cc, 4850m/sec; sensitivity to initiation,
PLX. A liq expl developed at PicArsn (Picatinny Liquid Explosive) during WWII for use in minefield clearing devices, to be loaded by pumping. It consisted of Nitromethane 95 and ethylene-diamine 5%, which were stored and transported separately, and mixed just prior to use. PLX is a light yel liq; OB to CO₂ -48.0% (vs -39.3% for straight Nitromethane); OB to CO -21.0% (vs -13.1% for straight Nitromethane); d 1.12g/cc at 20°. Its expl props, as detd at PicArsn, were as follows:
Ballistic Mortar. 134% TNT
Briscane (by Sand Test). 50.6g crushed vs 8.1g for straight Nitromethane and 48.0 for TNT
Explosion Temperature (5 sec). 430°
Friction Sensitivity. With BuMines Friction Pend app, unaffected
Impact Sensitivity. 100+cm with BuMines app using a 2kg wt; 20" with PicArsn app using a 2kg wt
Rifle Bullet Sensitivity. Unaffected from the action of .30 cal bullets fired from a distance of 90 ft
Trautz Test. 127% of PA
Velocity of Detonation. 6165m/sec as detd in a glass tube 15/16" diam and 1/32" wall thickness; vs 6210m/sec for straight Nitromethane
PLX corroded brass, but did not affect stainless steel, mild steel, or duriron

PNL. See under D-1 in Vol 3, D1-L

Pohl's Powder (Polvora blanca de Pohl). A Span expl resembling Augendre Powder (see Vol 1, A507-L) in compn. It contained K chlorate 49, K ferrocyanide 28, and sugar 23% Ref: Pérez Ara (1945), 23

Pobeditly. See under Coal Mining Explosives, Russian Permissible Explosives, in Vol 3, C454-R

Poisoning by Explosives. See under Toxicity

P.O.L. Ger: acronym for Pulverohe Lösung, which means Solventless Powder

Polar Ajax. A Brit Permitted Expl contg NG (+ Nitroglycol) 25.5–27.5, NC 0.25–1.25, AN 39.0–42.0, Na chloride 23.0–25.0, carbonaceous material 2.5–4.5, china clay 2.0–3.0, and other ingredients 1.0–2.5%. D 1.55g/cc; power (% Brit Gelignite, as detd by BalMort) 56. It is a plastic expl, and has been used in drifting, ripping and blasting hard coal. See also Vol 3, C452 & C453

Polar Dynabel No 2. A Brit Permitted Expl contg NG (+ Nitroglycol) 13.0–15.0, NC 0.25–0.75, AN 60.0–63.0, Na chloride 15.0–17.0, carbonaceous material 3.5–5.5, china clay 0.1–1.1, and other ingredients 0.5–2.0%. D 1.12g/cc; power (% Brit Gelignite, as detd by BalMort) 62. It is a cohesive powder, and has been used in drifting, ripping and blasting hard coal

Cartridges of this expl are usually sheathed in the following manner: each waxed cartridge of Polar Dynabel No 2 is placed in a larger paper cylinder, and the annulus between the cartridge and the outer cylinder is filled with a sheathing compd contg a dry, finely divided mixt of 1 p Na bicarbonate and 0.33–2.0p of a material composed of 61% commercial Al oxide and 39% chalk, both ground to pass 150 mesh
(Brit Standard Sieve). See also Vol 3, C452 & C453

Polarite. A Brit expl introduced prior to WWI as a substitute for Gellignite. It consisted of non-freezing Gellignite contg TNT, in which K perchlorate replaced K nitrate
Refs: 1) Marshall 1 (1917), 384 2) Barnett (1919), 111

Polar Thames Powder. A Brit Permitted Expl contg NG (+ Nitroglycerol) 9.0–11.0, AN 59.5–62.5, Na chloride 18.0–20.0, carbonaceous material 7.5–9.5, china clay 0.1–1.1, and other ingredients 0.1–1.1%. D 0.98g/cc; power (% Brit Gellignite, as detd by BalMort) 56. It is a granular material and has been used in moderately hard ripping and blasting operations of hard coal. See also Vol 3, C452 & C453

Polar Viking. A Brit Permitted Expl contg NG (+ Nitroglycerol) 9.0–11.0, AN 68.5–71.5, Na chloride 9.0–11.0, carbonaceous material 7.5–9.5, and china clay 0.1–1.1%. D 0.98g/cc; power (% Brit Gellignite, as detd by BalMort) 66. It is a granular material and has been used in moderately hard ripping and blasting of hard coal. See also Vol 3, C452 & C453

Polaris Missiles. US nuclear delivery system (UGM-27 series). A solid proplnt two-stage missile developed by Lockheed for the US Navy, designed to be fired from a submerged submarine, and first fired in 1958. Forty-one nuclear-powered submarines are currently in service (Ref 1), each carrying 16 ballistic missiles of the Polaris series. The initial Polaris A1 (UGM-27A), which became operational in 1960, has been phased out. The A2 (UGM-27B) equips about 10 submarines, while the remainder have the improved A3 (UGM-27C). A comparison of specifications for the latest 2 versions are shown in Table 1
The new Poseidon (qv) missile with MIRV multiple warheads will eventually equip 31 of the 41 submarines

Polis Explosive. A mixt contg Nitrotoluene and Pb nitrate as basic ingredients, which could be expld by heating
Refs: 1) Daniel (1902), 635 2) Gody (1907), 576

Pollard Explosive. A mixt of S, paraffin, and either a nitrate or chloride
Ref: Daniel (1902), 635

Pollard’s Test for Stability of Propellants. This test, proposed in 1924–25, is based upon the action of nitric peroxide on colloidal Ag oxide
Procedure. A current of air is passed over a sample of proplnt in storage into a colloidal sohn of Ag oxide. If free nitrogen peroxide is present, it reacts with the colloid and decreases the amt of light diffused by it. The larger the decrease, the higher the amt of NO₂ present, and the more decompd is the proplnt
Ref: Reilly (1938), 80

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<th>Polaris Missile Specifications</th>
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<tr>
<td>UGM-27B (A2)</td>
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<td>UGM-27C (A3)</td>
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POLLUTION ABATEMENT IN THE
US MILITARY EXPLOSIVES AND
PROPELLANTS MANUFACTURING INDUSTRY

Virtually all of the HEs and most of the
propionts for all three Services are manufd in a
network of Army Ammu Plants (AAPs) scat-
tered mainly over the eastern and southern
portions of the country. They are loaded in
other facilities of the same AAPs, in other
AAPs which do not themselves manuf chemicals,
and in a series of Naval Ammu facilities (NADs).
Two Navy facilities manuf some supplementary
ingredients, notably NG and casting powder;
but mostly they load expls obtained from the
AAPs.

The map in Fig 1 shows the distribution of
the AAPs and NADs which do the bulk of the
high expl and propiont manuf and loading.
There are approx as many more which deal in
small arms or metal parts or serve as storage
depots, but they are outside the scope of this
article. There are also several AAPs which load
warheads but do not manuf the fills; they are not
discussed in any detail in this article because
their relatively minor wastewater problems are
well typified by those facilities which are dis-
cussed

Major Steps in the Manufacture of Munitions.
The manuf of end item munitions can be divided
into four major steps: a) manufacture or pur-
chase of ingredients such as NC, NG, TNT,
HMX, binders, etc; b) combination of ingredi-
ents into blends, grains or formulations, such
as cannon powder, Comp B, extruded double-
base propiont grains, etc.; c) loading of warheads,
bombs, rocket motors, etc, with the blends or
formulations; and d) final assembly and pack-
out of complete munitions, including metal
parts

Manufacture of Ingredients. The manuf of chem
expls and propionts such as TNT or NC is com-
pletely similar to any other chem manuf opera-
tion; and the plants are much like any other chem
plant except that they tend to be more isolated from
their neighbors, more spread out within their own
fences, and rather less modern than average. They
are isolated and spread out for safety, since their
products are hazardous materials; and they are
less modern than most chem plants because they
tend to be rather old. That last factor is chang-
ing rapidly at this writing. A massive moderni-
ization program is underway, spurred by the need
to reduce air and w pollution but also taking
full advantage of opportunities to improve pro-
duction rates and efficiency by the installation of
new and modern equipment

A typical chem manuf operation is the pro-
duction of trinitrotoluene — TNT, the dominant
mil expl. It involves the manuf of huge quanti-
ties of nitric and sulfuric acids, from sulfur and
ammonia, in chem plants exactly similar to those
which make nitric and sulfuric acids in the civilian
economy. Mixed nitric and sulfuric acid is then com-
ined with liq toluene in a series of reaction kettles
to produce mononitrotoluene, dinitrotoluene,
and finally trinitrotoluene which is a solid.
The trinitrotoluene is separated from the mother
liquor, washed with w, and then treated with a
sulfite soin called "Selite" which extracts un-
derable isomers and impurities, leaving purified
α-TNT. The TNT is washed, solidified, flaked,
and finally shipped out in boxes

The operation is a thoroughly typical chem
manuf operation not unlike those found in the
plastics, petroleum, food, paint or solvents indus-
tries. It involves pumping of liqs, stirring of
 slurries, heating and cooling of streams, filtra-
tions, evaporations, dryings, bagging and boxing,
and all the other usual chem manuf operations.
It also involves wastewater streams containing
unreacted material and by-products, waste acids,
decompproducts and extracted impurities,
and exhausted reagents. These wastewater
streams, if untreated, constitute major pollution
problems

The manuf of NC is similar in that it involves
the same nitrating acids as used for TNT, but
used to treat cotton linters or wood pulp (raw
cellulose) in a series of vats and reactors similar
to the ones used for TNT. The crude NC is
similarly subjected to a series of w and aq soin
washes until it is finally delivered as a purified,
fibrous mat — ordinarily wet with w or alc for
safety. Again, there are major wastewater
streams laden with spent reagents and extracted
impurities

Tetryl, HMX, RDX, NG, and a whole host of
minor ingredients are all made similarly — in
typical chem process plants with typical equip-
Fig 1  Major Explosives and Propellant Facilities in the USA
ment and controls and typical wastewater streams

Production of Grains or Blends. Most expts and all propmts are blends of ingredients rather than single substances. Comp B, for example, is an intimate mixt of 60% RDX and 40% TNT, with a little wax added for stability. It is normally made in the RDX plant by blending in TNT and wax right on the production line without ever storing the RDX. There are four different Cyclotols, which are blends of RDX/TNT without wax: 75/25, 70/30, 65/35, and 60/40; and there are two Octolts, blends of HMX/TNT: 70/30 and 75/25. They are also made on the RDX/HMX line. There are dozens of other formulations incorporating other ingredients such as Tetryl, Al powder, PETN, etc. Most of them are made in the chem manuf plant and shipped to the loading plant as flakes or chunks, but some of them can also be made up in the meltmix kettles in the loading plant.

NC and NG are rarely used singly, but are usually incorporated into double-base or multi-base propmts which may have up to a dozen other ingredients including metal powders, oxidizers and various stabilizers and burning rate catalysts. The propmts are processed into shapes which range from pinhead size pellets to cylinders two or three feet in diameter and six feet or so long. The pellets may be used as is as gun propmts, or they may be incorporated into still more complex formulations in the casting of large rocket motors. The larger cylinders are usually complete rocket motor grains themselves, ready to be inserted into finished rocket motor hardware.

A small but important class of formulations comprises the Composite Solid Rocket Propellants. Composites typically contain a major amount of an oxidizer such as AP or HMX, a metal powder such as Al, a binder which is one or another type of rubber (or double-base), and up to a dozen trace ingredients such as catalysts, stabilizers, etc. There are literally hundreds of formulations, all to a degree similar; and the choice comes down to specific missions, economics, and special requirements.

Loading of End Items. The blends and formulations described above may be loaded into their hardware in the plant where they are made, or they may be shipped to another plant for Load/Assemble/Pack (LAP). There are a number of AAPs which are solely LAP plants, and four of the six Navy plants engage only in LAP.

Most current exps lists are blends of TNT with other ingredients, and are melt-cast loaded into bombs and warheads. Typically, several thousand pounds of the flaked blend are charged to a stirred melt kettle and heated to just above the melting point of TNT. It forms a mobile slurry when molten, and is poured into the empty bomb or shell cases, where it solidifies. Additional ingredients such as Al may be added in the melt kettle, depending on the particular formulation being poured and the particular munition product.

Small rocket motors are usually, but not always, loaded with pre-shaped double-base grains which are simply slipped into the motor case like a battery into a flashlight. Large motors are usually, but not always, loaded with a cast-in-place, composite grain which is mixed in special kettles and poured into the motor case to harden. An alternate loading method is to fill the motor case with tiny, loose, double-base pellets and then infuse the bed with a Casting Solvent consisting of NG and/or similar other energetic solvents for double-base. The solvent semi-dissolves the pellets and blends the whole into a tough, rubbery mass of adequate mechanical strength. Both the pellets and the casting solvent can, of course, have numerous other, minor ingredients. There are enough exceptions and overlapping cases to disprove any manufg classification; for example, pre-formed, slip-in grains are also used for certain rocket motors up to a couple of feet in diameter, which is quite large by most standards.

There is also an as-yet small but growing class of formulations known as "PBX", Plastic Bonded Explosive. PBXs are similar to rubber-base, composite rocket procepts in that they consist of 85% or so of powdered high-energy explosive incorporated into a "plastic" matrix which can be a conventional plastic or a double-base and cast into place.

Final Assembly and Pack-Out. The loaded warheads, rocket motors, etc., are finally assembled with their cases, electronics, etc., into finished munitions. This "dry" assembly involves no wastewater effluents.
Wastewater Streams — Sources and Types. The greatest number of AAP w pollutants (or potential pollutants) are similar to those from any chem manufg operation, eg, acid drippings, solvent spills, rust, stack scrubber drainings, floor washdown, and the like; but an important few are military-unique, eg, "Red Water" from TNT purification and w solns of various expls themselves. They are discussed briefly here under four headings,

1. **Acid Manufacture.** Relatively small; mostly leakage plus drainings from air pollution abatement scrubbers. Also included are: a) acid waters, neutralized with lime or soda ash; b) sometimes azeotroping agents such as n-propyl acetate; c) sometimes heavy metals from equipment corrosion; and d) nitroso bodies from acid recovery

2. **Basic Explosives Manufacture.** The major quantities and the toughest problems are here. They include: a) acid waters, treated with lime or soda ash, chemical washes, spills, washdowns; b) "Red Water" from TNT purification. A complex, brick-red soln of Na nitrate, Na sulfate, Na sulfite, Na nitrite, and about 17% organics which include sulfonated nitrotoluene isomers and complex, unidentified dye-bodies; c) dissolved expls, eg, "Pink Water" which is approx 100ppm TNT in w; d) suspended expl particles — dust and chips; and e) sometimes solvents such as acet, benz, and dimethyl aniline

3. **Compounding of Explosives and Propellants.** Small. Generally similar to streams from manufg, except that the chem purification wastes are absent. They include: a) dust and chips; b) dissolved expls, generally a few to 100ppm; c) solvents; d) organic materials such as collagen; and e) AN or AP

4. **Load/Assemble/Pack Operations (LAP).** Small. Mostly floor washdowns and generally similar to Pink Water. They include: a) dissolved expls; b) dust and chips; and c) heavy metals from paints and corrosion and metal cleaning. The washout of reject munitions at some LAP plants can contribute substantial additional effluents when washout operations are running

Table 1 summarizes — and oversimplifies for clarity and emphasis — the most characteristic wastewater problems of each of the products or operations highlighted in Table 2. Every operation has some aspects of every problem, but these are the outstanding ones. The major problems are the large volume, high concn, chem wastes from the manufg operations; the streams from acid manuf and loading operations are much smaller and much simpler. The most noticeable waste streams are the Red Water and Pink Water from TNT manuf and loading, respectively

Pink Water is simply a soln of TNT in w. α-TNT is sol in w to the extent of approx 100 ppm at ambient conditions, the exact value depending strongly upon temp and the presence or absence of other solutes. Freshly-made-sols of TNT in w are virtually colorless; but exposure to ultraviolet light, including sunlight, causes the formation of highly-colored, complex, incompletely identified substances similar to dyes. They impart a characteristic pink color which persists even after dilution down to a few ppm with clean w. The release of Pink Water to receiving streams is thus objectionable. Pink Water is ubiquitous where TNT is made or handled, because of the need to wash down equipment and working areas from time to time. The largest volumes and the highest concns are found in plants which manuf TNT or unload it from obsolete warheads, but it is also the major component in the (relatively small) wastewater streams from loading plants. There are a number of technically feasible approaches to removing dissolved TNT and the derived dye bodies from wastewaters, and one or another is planned for each installation with the problem

Red Water — which can be almost black at times — also contains dissolved TNT; however, it is not an incidental stream like Pink Water; it is a major by-product stream from TNT manuf. The mixed-acid nitration of toluene yields not only 2,4,6-trinitrotoluene, the desired product, but also a host of other isomers and by-products amounting to approx 4.5% of the total yield; and it is necessary to remove them from the product. They are removed by extraction with a Na sulfite—Na carbonate soln which sulfonates and dissolves them; the extract is called Red Water. Red Water is a very complex and somewhat variable mixt containing 15% or so of sulfonated or sulfitated nitroso bodies and a number of inorganic salts. Typical components are: w, Na₂SO₃—NaSO₄, NaN₂O₃—NaNO₃, sulfonated or
<table>
<thead>
<tr>
<th>Wastes</th>
<th>Trinitrotoluene &amp; DNT</th>
<th>Tetryl</th>
<th>Primer materials</th>
<th>RDX/HMX</th>
<th>Nitrocellulose</th>
<th>Nitroglycerin</th>
<th>NC-based propellants</th>
<th>Black Powder</th>
<th>Acid manufacture</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid waters, nitrate &amp; sulfate salts, etc.</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
<td>+</td>
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<tr>
<td>Red Water</td>
<td>+</td>
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<td></td>
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<td></td>
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<td></td>
<td>+</td>
<td></td>
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<tr>
<td>Pink Water</td>
<td>+</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Other dissolved explosives and/or dust and chips</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Organic solvents and resins</td>
<td>+</td>
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<td></td>
<td>+</td>
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<tr>
<td>Chromium and other metals from corrosion</td>
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<td></td>
<td></td>
<td>+</td>
<td>+</td>
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<tr>
<td>Perchlorate and other oxidizers</td>
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</tbody>
</table>

The above discussion has purposely been presented from a chem viewpoint in order to give a feel for the origin and nature of the wastewater streams. It has been usual to describe them in the conventional terms of BOD, pH, suspended solids, etc, and most of the surveys and permits are couched in these terms, although specific, military-unique parameters would be preferable.
### Table 2
The US Military Explosives and Propellants Industry

<table>
<thead>
<tr>
<th>Army Ammunition Plants</th>
<th>Activity</th>
<th>Product Capabilities</th>
<th>Ingredients Used in Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MFRE*</td>
<td>LAP**</td>
<td>Acid</td>
</tr>
<tr>
<td>Badger</td>
<td>Expls</td>
<td>Proplnts</td>
<td>+</td>
</tr>
<tr>
<td>Corbehnster</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Holston</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Iowa</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Indiana</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Joliet</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Kansas</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Louisiana</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Lake City</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Longhorn</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Lone Star</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Milan</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Newport</td>
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<tr>
<td>Radford</td>
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</tr>
<tr>
<td>Redstone</td>
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</tr>
<tr>
<td>Sunflower</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Volunteer</td>
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<table>
<thead>
<tr>
<th>Navy Ammunition Plants</th>
<th>NAD Crane</th>
<th>NAD Hawthorne</th>
<th>NOS Indianhead</th>
<th>NAD McAlester</th>
<th>NIROP Magna</th>
<th>NWS Yorktown</th>
<th>Al</th>
<th>AP</th>
<th>C4Cl2</th>
<th>DNT</th>
<th>HMX</th>
<th>NC</th>
<th>NG</th>
<th>NGa</th>
<th>NH4NO3</th>
<th>Ammonium Picrate</th>
<th>Polynitrate</th>
<th>Polyoxymethylene</th>
<th>PXD</th>
<th>PXX</th>
<th>TXN</th>
<th>WN</th>
<th>WNO3</th>
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</thead>
<tbody>
<tr>
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</table>

<table>
<thead>
<tr>
<th>Air Force Ammunition Plants</th>
<th>Plant 44</th>
<th>Plant 77</th>
<th>Plant 78</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

* Manufacture
** Load/Assemble/Pack

**Munition Plant Modernization Program.** Both the US Army and the Navy have extensive plant modernization and pollution abatement programs planned and underway, and the wastewater picture is changing rapidly. So rapidly, in fact, that field data are out of date by the time they can be put into a report. Perhaps the best way to present the story is to force-fit all information into one of three time eras:

*Before Modernization.* Manufg processes from the early 40's to the late 60's. In general, this meant little or no pollution awareness or abatement, with things like Red Water being discharged directly into rivers; and effluent characterization was essentially a description of the raw process discharges.

*Transition Period.* The past few years, today, and the next few years, while new treatment processes are being developed and installed. Presentday plants exhibit a mixed picture of modern abatement facilities alongside antique process units, and effluent streams range from...
raw discharge to zero discharge. New construction is everywhere, and even more construction is in the planning stage. Research and development is in progress on even better abatement processes. Consequently, even current wastewater data have only the most limited significance except as trend indicators

*After Modernization.* That day in the future (1980's) when all the planned installations are complete and on stream. There will still be a few problem areas then, but by and large, the military munitions plants are planned to be models of clean outfalls. Those effluent data will be the first to be truly indicative of state-of-the-art or best-available

*Note:* This article is abstracted from a comprehensive state-of-the-art study of the military expts and proplants production industry and its pollution abatement problems and programs, carried out by an ad hoc committee of the American Defense Preparedness Association for the Environmental Protection Agency. A comprehensive report authored by Col. Norman I. Shapira (USA, Ret), Drs James Patterson and John Brown, and Messrs William Duckert and Jack Polson is available from the National Technical Information Service, Springfield, Virginia 22161, in two volumes: EPA-600/2-76-213a and EPA-600/2-76-213c. (EPA-600/2-76-213b is a third volume which has not been published)

*Written by J.A. Brown*

*Refs:* 1) R. Eliassen, "Wartime Operating Problems in Municipal and Army Sewage Treatment Plants", *SewageWorksJ 16*, 363 (1944)


9) W.A. Bullerdek, "Removal of TNT from Waste Water Using a Solvent Extraction Process", *TechRept 89*, Burlington AEC Plant (1964)


14) D. Griffin, "Joliet Army Ammunition Plant Pollution Discussion and Abatement Plans", *PATR 4368* (1972)


21) J.W. Patterson & R.A. Minear, "State-of-the-Art for..."

Ólvoras Negras (Span for BlkPdrs). Fairly detailed description of Span method of manuf is given by Sancho (Ref, p 264). The sources of the charcoal used were stems of hemp (tallos de cáñamo), of flax (lino), of oleander (adelfa), of yew-tree (tejo), etc. Following, in Table 1, are given typical compts of some Span BlkPdrs

Table 1
Composition of Typical Spanish Black Powders

<table>
<thead>
<tr>
<th>Powder of the Fábrica de Murcia</th>
<th>Nitrate</th>
<th>Sulfur</th>
<th>Charcoal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infantry powder</td>
<td>80.0</td>
<td>15.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Artillery powder (fine grains)</td>
<td>75.0</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Artillery powder (6 to 10mm grains)</td>
<td>78.0</td>
<td>10.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Prismatic powder (with 1 or 7 perforations)</td>
<td>74.0</td>
<td>10.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Prismatic powder (brown)</td>
<td>80.0</td>
<td>3.0</td>
<td>17.0</td>
</tr>
</tbody>
</table>

See also under Black Powder or Gunpowder in Vol 2, B165-R ff
Ref: Sancho (1941), 253–85

Ólvara Progressiva de Fusil Tipo “G”. A Span propInt contg NC 97.75, DPHA 0.75, Na oxalate 1 (the latter two serving as stabilizers), graphite 0.1 (surface), and volatile matter 0.4%. Its manuf and properties are described in the Ref
Ref: Vivas, Feigenspan & Ladreda 3 (1948), 225–393

Polyacetylenes (or Polynyes). See under “Acetylenic Condensation and Polymerization Products” in Vol 1, A62-L to A63-L. Selected polyacetylene expl comps as an adjunct to these are presented below, as well as addnl refs

Diacetylene or Butadiyne and Its Silver Salts. See Vol 5, D1120-L

Diacytlenic Dihydroperoxides. See Vol 5, D1120-R

Dichloroacetylene or Dichloroethyne. See Vol 5, D1203

1,6-Dichloro-Hexa-2,4-diyne. CH₂CL.C.C.C.C.CH₃Cl; mw 147.00; liq; bp 61° at 0.5mm; d 1.219g/cc; RI 1.5750. Prep is by reacting hexa-2,4-diyne-1,6-diol with thionyl chloride in py. Explnds on distn
Ref: Beil, 1 (1119)
Diiododiacetylene or Diiodobutadiyne. See Vol 5, D1298-L

1,8-Dimethyloctaacylene.
CH\(_2\)C\(\cdot\)C\(\cdot\)CH\(_2\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)H\(_2\); mw 222.24; OB to CO\(_2\) –280.78%; white ndls turning brn at RT; mp, explds below mp. Prep is by reacting methylidiacetyleneMgBr in eth under N\(_2\) with dry Cu chloride. The mixt is exptd with aq ammonium chloride, concd to 100ml and cooled to –78\(^\circ\). The crude yield is purified by chromatography on AI oxide using 1:2 eth-petr eth as the eluting agent.
Refs: 1) Beil—not found 2) H.H. Schlubach & V. Franzen, Ann 572, 116–21 (1951) & CA 45, 10206 (1951)

1,8-Diphenylbutylacetylene.
C\(_6\)H\(_5\).C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)H\(_2\); mw 250.30; OB to CO\(_2\) –287.65%; fine yel ndls; mp 113\(^\circ\).
Prep is by reacting phenylidiacetyleneMgBr in eth under red light with Cu chloride. Purification of the crude ppt involves filtration, washing with aq ammonium chloride, evapn to 100ml of soln, soln in 4:1 lgr-benz, followed by chromatography on Al oxide. The polyacetylene compd is stable in the dark at RT. It explds on rapid heating.
Refs: 1) Beil—not found 2) H.H. Schlubach & V. Franzen, Ann 572, 116–21 (1951) & CA 45, 10206 (1951)

1,16-Diphenyloctaacylene.
C\(_6\)H\(_5\).C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)H\(_2\); mw 346.38; OB to CO\(_2\) –281.77%; red ndls; decmps in the dark at 20\(^\circ\) within a few hrs after prep. Prep is by condensing \(\alpha\)-bromocinnamaldehyde with penta-2,4-diyne-1-ol. The cryst glycol formed is first converted to the dichloride (using thionyl chloride), then to the monophenylbutylacetylene using Na amide and finally to the diphenyloctaacylene by treatment of the monophenyl compd with Cu chloride and oxygen. The prod explds on touch or on attempts to heat it.

1,10-Diphenylpentaacylene.
C\(_6\)H\(_5\).C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)C\(\cdot\)H\(_2\); mw 274.32; OB to CO\(_2\) –285.80%; yel cryst; mp, stable at 0\(^\circ\), brn at 60\(^\circ\), then blk and explds at about 160\(^\circ\). Sol in benz and petr eth. Prep is by reacting under red light diethynylMgBr with phenylacetylene-aldehyde at –15\(^\circ\) in eth. The mixt is allowed to reach RT and stand for 12 hrs. The cryst prod of this step is further treated with ammonium chloride, then thionyl chloride at –10\(^\circ\). The next step involves pptn of the crude yield of diphenylpentaacylene with K ethanolate under nitrogen. The crude yield is purified by repeated chromatography using petr eth-benz eluant. The final yield is 6.1%

Iodobutadiyne (Iododiacetylene).
CH\(_2\).C\(\cdot\)C\(_2\).Cl; mw 175.95; OB to CO\(_2\) –40.92%; cryst; mp ca –40\(^\circ\); bp 71\(^\circ\); d 1.824g/cc at 15/4\(^\circ\); RI 1.5058. Prep is by reacting one mole of iodine with acetylene-bis-Mg bromide in eth. The compd is sens and will expld at temps over 30\(^\circ\)
Ref: Beil 1, [246] & [1117]

Hexa-1,5-diyne (Bipropargyl or Dipropargyl).
HC\(_4\).CH\(_2\).CH\(_2\).C\(\cdot\)CH; mw 78.12; OB to CO\(_2\) –307.22%; mp –4.27\(^\circ\); bp 87.86\(^\circ\); d 0.788 g/cc; RI 1.43934. Sol in eth; insol in w. Prep is by reacting monosodiumacetylene with 1,2-dibromoethane in a mixt of dimethyformamide and tetrahydrofuran at 30\(^\circ\). Bipropargyl explds violently when heated to 110–20\(^\circ\)
Ref: Beil 1, 266, [128], [247], [1057]& [1118]

Hexatriyne (Triacetylene).
HC\(_3\).C\(\cdot\)C\(\cdot\)C\(_2\).CH; mw 74.08; OB to CO\(_2\) –280.78%; liq; mp –20\(^\circ\). Sol in acet. Prep is by reacting 1,6-dichloro-hexa-2,4-diyne with Na hydroxide in eth. Hexatriyne explds in air at 0\(^\circ\). It is stable under nitrogen and in air at –20\(^\circ\), but its polymer, which exists below its mp, can be expld by touching it with a glass rod. Its silver salt, Di silver hexatriyne, Ag\(_2\)C\(_6\), can also be expld by touch
Ref: Beil 1, [1070] & [1141]
Penta-1,3-diyn (Methyldiacetylene).
CH$_2$C=C:C=CH; mw 65.10; OB to CO$_2$
-294.93%; liq; mp -4.5° to -38.5°; bp 76–77°
(expids at atm press), 45° at 140mm; d 0.7909
g/cc at 20/4°C; RI 1.4762 (Ref 3) and 1.4817
(Ref 1). Sol in ethanol and petr with a bp
> 180°. Prepn is by reacting monosodium
acetylene with dichloromethane in liq am
monia at 20 to 40°, followed by treatment with
ammonium chloride. The product is stable in
the dark at -35° but polymerizes readily at
above -20° in the light. Penta-1,3-diyn forms
two expl salts: Copper penta-1,3-diyn, CuC$_2$H$_3$,
dark yel nds, by reaction with Cu, explds
on shock or by rubbing; and Silver penta-1,3-
diyn, yel-brn nds, by reaction with Ag silver
nitrate in ammonium hydroxide, a v expl compd

Reps: 1) Beil 1, [247], [1057] & [1117]
(1950) & CA 44, 8313 (1950)
3) L. Brandesn, "Preparative Acetylene Chemistry", Elsevier,
NY (1971), 35–6

2,2,23,23-Tetramethyl-tetracosa-7,9,15,17-
tetraene-3,5,11,13,19,21-hexayne.
(CH$_3$)$_2$C=C:C=CH:CH:CH:C=C:CH:CH:CH:C=C:C=C:CH_{3};
mw 362.54; OB to CO$_2$ -304.52%; yel cryst;
mp, explds at about 250°. Sol in eth and methanol.
Prepn is by reacting [8,8-dimethyl-7,11,17-triyn]-
triphenyl phosphonium bromide with butyl-
lithium in eth followed by propiolaldehyde.
The product of these reactions is then treated
with a mix comprised of a soln of 11,11-di-
dimethyldodeca-3,5,7-triene-1,7,9-triyne in metha-
nol and copper acetate in aq pyr

Reps: Beil 1, (1117)

Polyacrylates. See Vol 1, A96-R to A97-R
and the following limited and unlimited distribution
Hydrazine Heterogeneous Propellant Develop-
ment", ARFPL-TR-68-216, Contract AF-04-(611)-11606, Dow Chem, Midland (1968)
(limited)
2) J. Simicek, et al, "Explosive Acrylic Polymers",
Rept No FSTC-HT-23-
1046-73, AFSC TC, Charlottesville (1973)
3) R.P. Rastogi & K. Kishore, "Polymers as
Fuel Binders in Composite Solid Propellants",
JSciIndRes 32 (6), 282–99 (1973) & CA 80,
121565 (1973) (unlimited)
3a) L. Leneveu
& F. Villey-Desmeserets, FrP 2182663 (1974)
& CA 81, 51891 (1974)
4) L.B. Childs Jr
& J.D. Martin, "Rocket Propellant with Acrylate
Binder and Difluoroamino Plasticizer", USP
3933542 (1976) & CA 84, 138050 (1976)
(unlimited)

Polyalkylbenzenes, nitration of. See in Vol 1,
A129-R to A130-R and Addn Reps: 1) Urb-}

"Ski 1 (1964), 74–5
2) D.V. Nightingale,
ChemRevs 40, 117–40 (1947) & CA 41, 2687
(1947)

Polyamide Gels. Several mats of this type have
been invented for use in demolition charges for
concrete structures (Ref 1), or for incendiary
bombs and flame throwers (Ref 2). The former
consists of a slurry type expl conqg a clay that
swells when wet which consists of one or two
resinous plastics such as polyamides. The latter
consists of a suitable solvent such as petr eth,
ocetyl alc or acetophenone and a polyamide
prepd by reacting, typically, a mole of cetyl-
malonic ester with a mole of 1,3-diaminopropane.
These reactants give a waxy matl with an avg
mw of 2400 and a mp of 165°. The gel is prepd
by mixing the polyamide with one of the solv-
ents, heating the mixt to its bp and cooling to
25–30°

Reps: 1) D.E. Floyd, USP 2662068 (1953) &
CA 48, 4222 (1954)
2) T. Takayama, JapP
75-18052 (1975) & CA 83, 195956 (1975)

Polyamides. A plastic matl prod by condensa-
tion processes resulting in a chain polymer con-
sisting of repetitive amide groups. The best
known amide polymer is called generically,
Nylon. The mil uses for polyamides such as
Nylon are numerous and include adhesives,
airframes, armor, bearings, cements, foams,
greases, primer coatings for metals, projectile
coatings, ration packaging, rocket motor linings
and tires. A general use mil spec exists for
Nylon (Ref 1). For further information on
polyamides, see "PLASTEC" (a source of
appropriate publications) in this Vol, as well as
"Amides and Imides, Organic" in Vol 1, A170-R and the following

Polyamines. See under the various topics in Vol 1; viz, “Aminoethylcellulose (AEC) (Polyaminoethylated Cellulose)”, A203-R to A204-L; “Aminoethylcellulose Perchlorate (AECP) or Polyaminoethylcellulose Perchlorate”, A204-R; “Aminoethyl resorcinol (AEN) and its Perchlorate (AENP)”, A205-L; “Aminoethylpolyurethane (AEP)”, A205-R; “Aminoethylpolyvinyl Alcohol (AEVPA) and Its Perchlorate (AEVPAP)”, A205-R; “Aminoethylpolyvinyl Chloride (AEVPC)”, A205-R to A206-L; “Aminoethyl protein (AEP)”, A206-L and “Aminoethylstarch (AES) and Its Perchlorate”, A206-L and R. Also, the following limited distribution Addnl Ref: B.D. Strauss, “Development of Polyamine Nitrate Propellants”, PATM 2086 (1973)

Polyamyllose, Nitrated. See under “Amylose” in Vol 1, A398-R to A399-R

Polybenzyl, Nitrated. See Vol 2, B95-R under “Benzyl Chloride and Derivatives” and Addnl Ref: C.S. Marvel, OSRD 875 (1942)

Polybutadiene and its use as a Binder with Energetic Materials. For "Butadiene and Derivatives", see Vol 2, B365-R to B366-R. For “Composite Propellants”, including a general discussion of butadiene polymers, see Vol 3, C464-L to C474-L. A more specific and updated discussion of Polybutadiene follows

There are two types of Polybutadiene polymers used in ordn; viz, carboxyl terminated (CTPB) and hydroxy terminated (HTPB). The preferred polymer for energetic material binder purposes is the hydroxy terminated variety because of its low viscosity, hence ease of prepbn, and better ageing and burning characteristics than the carboxyl terminated variety.

(Refs 7, 8, 9, 10, 12, 13 & 15). Hence, information on HTPB is presented in some depth

Hydroxy-Terminated Polybutadiene (1,2-Polybutadiene or HTPB).

\[
\begin{array}{c}
\text{CH}_2 \\
\text{CH} \\
\text{C}=\text{CH} \\
\end{array}
\]

n; mw 11,600; the compd exists in several cryst structures whose properties are tabulated below (Ref 7a)

<table>
<thead>
<tr>
<th>Isotactic</th>
<th>Syndiotactic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(99%)</td>
<td>(98%)</td>
</tr>
<tr>
<td>Lattice</td>
<td>rhombohedral helical</td>
</tr>
<tr>
<td>Monomers/Unit Cell</td>
<td>2</td>
</tr>
<tr>
<td>MP, °C</td>
<td>126</td>
</tr>
<tr>
<td>Crystal density, g/cc</td>
<td>0.96</td>
</tr>
<tr>
<td>R1</td>
<td>1.5154</td>
</tr>
<tr>
<td>Solvents</td>
<td>benz, chl, pyr, toluene &amp; xylene</td>
</tr>
</tbody>
</table>

Hydroxyl terminated polybutadiene can be prepbd by an anionic polymerization technique (Ref 4) resulting in hydroxy groups terminating each end of the polymer chain. The process uses an isopropanol-solid carbon dioxide bath (−78 oC) contg a reaction vessel into which above stoichiometric amounts of tetrahydrofuran (900ml), lithium metal (0.217g), and naphthalene (4.204g) are introduced under argon, and then magnetically stirred for two days or until the lithium dissolves in the naphthalene. Gaseous butadiene (177g) is then slowly bled into the reaction vessel over a period of eight hours. Five ml of ethylene oxide is then quickly added to the mixt, prod a colorl gel. The reaction mixt is then warmed to RT and stirred for several days until the ethylene oxide penetrates the initial gel and the entire system is colorl and solid

Polybutadiene is used extensively in many expl and propnt comps. One such expl usage was patd by dePrisme et al (Ref 11). Here, HMX, PETN or RDX is used to comprise 40–80% of the compn which is formulated, for example, to include powd Al (43 parts) and graphite (0.2 part), along with one of the above expls (50 parts). This mixt is combined at 80° with 6.8p of a binder contg polybutadiene, dioctylazelate, nonylphenyl phosphate, Fe naph-
thlate, plus an epoxy resin. After mixing to a uniform particle suspension, the mass is allowed to solidify

According to Krowicki et al (Refs 1a & 5), a typical composite propel's compn consists of:

- a combustible component amounting to (on a wt basis) 10.5%, contg (by wt)
  - Butadiene/2-methyl-5-vinyl py (90/10) 100p
  - Flexamine 3p
  - Liq polybutadiene-plasticizer 25p
  - Light petroleum oil-plasticizer 25p
  - P-quinone dioxime 2p

plus 4mm perchlorate as an oxidizer (on a wt basis) 84.5%, and boron (on a wt basis) 5.0%

Manuf of these propelnts, according to Urbaniaki (Ref 2), is accomplished in steps:

a) Milling. The oxidizer is milled into granules with a particle size ranging from 5 to 500 microns. Fineness of the particles controls the rate of burning of the mixt

b) Mixing. The polybutadiene is mixed with such ingredients as carbon black, plasticizer, accelerator and inhibitor on rollers usually employed in the rubber industry. In the final mixing the oxidizer and combustion catalyst are added to the binder-fuel. This stage of mixing is usually accomplished within 2 hrs between rollers heated to 50–60°

c) Pressing. The hot, homogeneous mass is shaped in a hydraulically-operated extrusion press of the type used for smokeless powd's. It is usually cruciform. A guillotine cuts the extruded mat to the reqd length. The outer surfaces of the limbs of the cross are covered with a substance which does not burn readily (ie, strips of plasticized cellulose acetate or polystyrene, 1.5–5mm thick), and cemented in place to prevent uneven burning at the surface

d) Curing. The final operation in polybutadiene propelnt manuf is the curing of the binder. The shaped mat is put into a curing oven for 16–48 hrs at 70–110°. The temp and duration of this operation depend on the compn of the mixt, charge dimensions and the physical properties desired

The parameters of a typical polybutadiene–

- Amm Perchlorate propellant are presented next

(Ref 2):

- Burning under press (kg/cm²) 1–140
- Specific impulse $I_g$ at $P=70$ kg/cm² 250
- Rate of burning (mm/sec) under press $P=70$kg/cm² 11.9
- Exponent n in the eq $V = kP^n$ 0.236
- Density, g/cc 1.74

The most significant use for HTPB propelnts is in ballistic missiles (Refs 12 & 13). The most unique usage is in the functioning of a laser by means of the chemical exhaust species generated by a HTPB–Amm Perchlorate fuel matrix (Ref 9)

Some ordn uses have been found for carboxyl terminated polybutadiene; viz, as rocket motor liners for propelnt mixts contg HTPB (Ref 17) and as part of a terpolymer binder for propelnts (Ref 16)

The US military specification for polybutadiene is for the carboxyl terminated variety (Ref 1b). The requirements of this spec are listed below for Type I (low acid), Type II (high acid)
### Table 1

Chemical and Physical Requirements for CTPB

<table>
<thead>
<tr>
<th></th>
<th>Type I</th>
<th></th>
<th>Type II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Viscosity, Poise at 77°F</td>
<td>230</td>
<td>350</td>
<td>230</td>
<td>350</td>
</tr>
<tr>
<td>Viscosity Ratio, 77°F/100°F</td>
<td>1.5</td>
<td>3.0</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Specific Gravity, 60°F/60°F</td>
<td>0.890</td>
<td>0.925</td>
<td>0.890</td>
<td>0.925</td>
</tr>
<tr>
<td>IR, 25/D</td>
<td>1.514</td>
<td>1.519</td>
<td>1.514</td>
<td>1.519</td>
</tr>
<tr>
<td>Carboxyl Content, Wt %</td>
<td>1.10</td>
<td>1.40</td>
<td>1.60</td>
<td>1.90</td>
</tr>
<tr>
<td>Unsaturation Type</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cis (% of Total)</td>
<td>25</td>
<td>45</td>
<td>25</td>
<td>45</td>
</tr>
<tr>
<td>Trans (% of Total)</td>
<td>35</td>
<td>55</td>
<td>35</td>
<td>55</td>
</tr>
<tr>
<td>Vinyl (% of Total)</td>
<td>15</td>
<td>25</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Volatiles, Wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture, Wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antioxidant, Wt %</td>
<td>1.0</td>
<td>1.5</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Insol in Trichlorethylene, Wt %</td>
<td>0.2</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Ash, Ignited, Wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qc, BTU/lb net</td>
<td>17,900</td>
<td>18,400</td>
<td>17,900</td>
<td>18,400</td>
</tr>
</tbody>
</table>

Footnotes to Table 1:

- a — Detd by the use of a Model RUF Brookfield Viscometer, Brookfield Engng Labs, Stoughton, Mass
- b — Detd by calcd the ratio
- c — Detd using a pycnometer gravimetrically
- d — Detd by using a refractometer
- e — Detd by titration using Na methylate and a thymol blue indicator under nitrogen
- f — Detd spectrophotometrically using a Model 21PE infrared spectrophotometer
- g — Detd gravimetrically using a Risco rotating vac evap
- h — Detd by Karl Fischer titration
- i — Detd by differential UV spectrophotometry of alcoholic KOH saponified trichlorethylene sol CTPB using a Beckman DV instrument
- j — Detd gravimetrically by loss-in-wt after drying at 220°F for 30 minutes min
- k — Detd gravimetrically by loss-in-wt after ignition at about 1000°F for one hour
- l — Detd calorimetrically

References:

1. Beil, 1, (937–948)  
2. K. Krowicki et al, "Solid Rocket Propellants", StatePaluva-Rakietowe(Pol), Trmsin No HT6600730, TM 7000397, FTD, Wright Patterson AFB (1964)  
10. A.J. Dimolo et al, "Evaluation of The Mechanical and
11) F. Dubois de Prise et al, "Composite Explosive Containing a Synthetic Resin Binder", FrP 2109102 (1972) & CA 78, 99989 (1973)
17) G.F. Sieg et al, "Bonding a Rocket Motor Liner to a Solid Rocket Propellant Grain", USP 3904715 (1975) & CA 84, 7210 (1976)

Polybutene, Polybutylene, Polyisobutene, Polyisobutylene, Poly 2-Methylopropane, Poly γ-Butylene, Poly unsym Dimethylethylene or PIB. For "Butene and Derivatives", see Vol 2, B375-R to B376-L. For "Butene Polymer Dynamite", see Vol 2, B376-R. For the use of polyisobutylene in "Composition C Type Explosives", see Vol 3, C484-L to C488-R.

PIB exists either as a low mw (about 12,000) viscous or atactic liq or as a crys matl of about 100,000 mw. In this latter form the isotactic (chain) type configuration predominates over the atactic and amorphous forms (Ref 8). Since the isotactic form is the form designated by mil spec (Ref 2), its parameters are presented below; viz.,

\[
\begin{array}{cccc}
H & H & H & H \\
\text{C} & \text{C} & \text{C} & \text{C} \\
\text{H} & \text{CH}_3 & \text{H} & \text{CH}_3
\end{array}
\]

Cell or unit quantity = 2V(n); mw 99,000 to 120,000; color of rhombohedral crys; mp 135.5 to 141°; d 0.95 g/cc; the RI increment in n-heptane at 60° and 5460 m (\(\Delta n/d(m/g)\)) is 0.115. Sol in most inert hydrocarbons such as benz, ethylcyclohexane, n-nonane, n-heptane and decalin. Prepn is by reacting 1-butene in an inert hydrocarbon solvent such as benz with a polymerization catalyst such as Ti chloride or V chloride under an inert gas and at temps of from 20 to 100°. The reaction is deactivated at completion by w addn and the polymer is then thoroughly dried (Refs 3 & 8).

The prep of PIB binder for inclusion with energetic materials to form expls or proplnts is as follows (Ref 1a): Using a hot w-heated 100 gal Baker-Perkins mixer equipped with two sigma-shaped blades rotating to give a kneading action (the front blade is rotated at 15rpm and the rear blade at 30rpm) to perform the actual mixing, mix 354 lbs of di(2-ethylhexyl) sebacate with 96 lbs of SAE No 10 engine oil at 82-90°.

Next, add 75 lbs of sheet PIB in 4" x 4" x 1/16" pieces while continuing the agitation. Then cool to 25°, and add 12 lbs of n-hexane to decrease visc. Still agitating, incorporate an addn 150 lbs of PIB. Reheat the mix to 82-90° for an addn 10% hrs. Cool to 30°. Yield is 600 lbs.

Aside from the aforementioned uses of PIB in expls and composite proplnts, other uses have been found in proplnt igniters (Addn Ref 1) and explignition trains (Addn Ref 4).

A typical compn of plastic proplnt in which PIB is used is shown below (Ref 3); viz,

<table>
<thead>
<tr>
<th>Constituent</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium Perchlorate</td>
<td>78</td>
</tr>
<tr>
<td>Aluminum</td>
<td>10</td>
</tr>
<tr>
<td>Burning rate catalyst</td>
<td>1</td>
</tr>
<tr>
<td>Surface-active agent</td>
<td>1</td>
</tr>
<tr>
<td>PIB binder</td>
<td>10</td>
</tr>
</tbody>
</table>

"This compn has more than 79% by volume of solid constituents. Plastic proplnt is thus a very highly filled suspension and it is only possible for it to contain such a high proportion of solids if there is a wide, specially graded range of particle sizes. This grading is achieved partly by careful choice of starting material, and partly by breakdown of the solid particles during the manufacturing process.

"... In some compositions the PIB is plasticized with ethyl olate to improve low temp properties... Since the proplnt is a stiff paste it can be inserted into a rocket motor by a type of injection moulding process" (Refs 3 & 5).

In a recent patent of Bartley's (Ref 11), a PIB proplnt is described which has the following compn and properties:

**Composition**

<table>
<thead>
<tr>
<th>Rubber binder, %</th>
<th>11.13</th>
</tr>
</thead>
<tbody>
<tr>
<td>consisting of:</td>
<td></td>
</tr>
<tr>
<td>- Isobutylene (10-20%)</td>
<td></td>
</tr>
<tr>
<td>- Nitrate oxidizers (80-90%)</td>
<td></td>
</tr>
<tr>
<td>Ammonium Nitrate, %</td>
<td>79.03</td>
</tr>
<tr>
<td>Ferrous Oxide, %</td>
<td>1.09</td>
</tr>
<tr>
<td>Additives, %</td>
<td>8.74</td>
</tr>
<tr>
<td>Burning Rate at 80°F, inches/sec</td>
<td>0.14</td>
</tr>
<tr>
<td>Specific Impulse at 1000psi, lb sec/lb</td>
<td>200</td>
</tr>
</tbody>
</table>

Several dissadvantages to plastic proplnts contg PIB have been noted. One is the existence with certain formulations of combustion in-
stability at 1000 psi (Ref 4). The other disadvantage is dimensional instability, i.e., grains made using PIB binder do not retain their original form, and sag or dimensionally deform on storage. Also, in some instances, there is a noticeable tendency to harden and fissure upon ageing (Ref 9).

The US military specification (Ref 2) lists the following requirements for PIB: (1) stability against depolymerization at 125°F; (2) color—shall not be darker than a sohn of 0.008g/L of K2Cr2O7/w by visual comparison; and (3) chemical properties as shown in Table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Viscosity, centistokes a</td>
<td>3.15</td>
<td>3.72</td>
</tr>
<tr>
<td>Iodine No b</td>
<td>—</td>
<td>1.32</td>
</tr>
<tr>
<td>Chlorine, % c</td>
<td>—</td>
<td>0.10</td>
</tr>
<tr>
<td>Acidity (as HCl), % d</td>
<td>—</td>
<td>0.01</td>
</tr>
<tr>
<td>Insol Matter, % e</td>
<td>—</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Footnotes to Table 1:
- a Obt by using a No 1 Ubbelhode viscosimeter
- b Obt by Wijs procedure using KI and Na thiosulfate titrant solns
- c Obt colorimetrically using Ag nitrate soln with Nessler tubes
- d Detd by titration with std NaOH soln
- e Detd gravimetrically in a Gooch crucible after washing with xylene


Polycarbonates. Linear thermoplastic polyesters of carbonic acid with aliphatic or aromatic dihydroxy compounds. A general structure presentation is as follows (Ref 4):

$$\text{H}_2\text{ORO}-\overset{n}{\text{C}}\text{OROH}$$

The most widely used monomer compd is 2,2-Bis (4-hydroxyphenyl)-propane or bisphenol-A. For a description of this monomer see Vol 2, B147-R. The properties of the polymer or resin comprised of this monomer are presented next:

$$\begin{pmatrix}
\text{CH}_3 & \text{O} \\
\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{C.O.} \\
\text{CH}_3 & \\
\end{pmatrix}_{n}$$

transparent amorph solid; mp 268°; d 1.20g/cc; RI 1.586. Sol in sym-tetrachloroethane, methylene chloride, cis-1,2-dichloroethylene, chlf and 1,1,2-trichloroethane; insol in acet, eth and carbon tetrachloride. Prep is by reacting bisphenol-A dissolved in py with phosgene in the following manner (Ref 1a):

“Twenty-three grams (0.1 mole) of bisphenol-A are dissolved in 200ml of pyridine in a vigorously stirred flask provided with a cooling bath to maintain the temperature at 25–35°. Phosgene is introduced into the reaction mixture thru a wide-bore tube at a rate of 1.0g/min. After 7 to 8 minutes the reaction mixt is saturated with pyridine hydrochloride and pptn may start. About ten minutes after the start of the reaction the mixt is too thick for convenient stirring. The polymer may be recovered by the addition of methanol or other solvents which will dissolve the pyridine hydrochloride and ppt the polymer.” The yield is essentially quantitative and the polymer will have an intrinsic viscosity of (about) 79,000 to 674,500 poise measured in dioxane at 30° (Refs 1a & 4)

Polycarbonate resins can be cast or injection molded. They possess a high degree of thermal stability and undergo little decomps below 250°. They can be mixed with fiberglass for addnl strength. Techniques of fabrication and copolymerization are presented in refs 1 thru 8, as well as prolonged weathering effects (Ref 6a). See also under “Epoxy Resins or Epoxies” in Vol 5, E106-R to E107-L

Polycarbonates have wide applications in ordn. However, the applications which are of special interest here are used as various types of armor (Ref 3, 5 & 8) and as pyrot binders (Ref 6 & 7)

The need for transparent airframe areas such as radardomes, ballistic surfaces or impact shields has resulted in a thorough investigation of the utility of polycarbonates in this area. The work of Ball et al (Ref 3) shows that a high-clarity polycarbonate can be fabricated by injection molding and that ballistic properties are not related to low rate (Izod) impact but to homogeneity, i.e., a single homogeneous plate of polycarbonate is superior in ballistic performance to multiple plies of the same material. Belkin et al (Ref 5) noted that, “. . . In addition to their high specific impact strength, polycarbonates are characterized by their rigidity, hardness and elasticity. As opposed to many other plastics, polycarbonate laminates do not shatter on impact. This property makes it fit the needs in many cases of the defense industry.” Specific usage in critical aircraft transparencies is noted by Voss in Ref 8, i.e., windshields and canopies for the F-15 and YF-16 fighters, and bird-proof windshields for T-37 and A-37 aircraft. Extensive service use has revealed only one significant problem area, namely surface scratch and erosion protection. The currently developed soln to this problem involves direct fusion cladding of an erosion and scratch-resistant polyurethane layer onto the surface of the polycarbonate

The work of Hamermesh and Witucki (Refs 6 & 7) on pyrot polycarbonate binders is of interest. As reported in Ref 6, the authors prep a polyalkyl carbonate by the reaction of a glycol with phosgene:

$$\text{O} \quad \text{O}$$

$$\text{HO.R.OH + Cl}_2\text{CICl} \rightarrow \text{H.(O.R.O.C.)_n OR.OH.}$$

At 70–80° the yield is 55–75%. The binder is cured at 160°F for 72 hrs. Because the polymer
is a liq of 32,000cps visc before cure, a polyisocyanate cross-linker is used. The binder is incorporated with standard pyroflare and signal ingredients (Refs 6 & 7)


Polydiamides. See under “Diamides” in Vol 5, D1125-L and R

Poly (Difluoroamino)-Substituted Cyanuric and Isocyanuric Acid Derivatives. For Cyanuric Acid and Derivatives see Vol 3, C589-R ff. For “Difluoroamino Compounds” see Vol 5, D1258-L

Of particular interest is Tris[1,2-Bis (Difluoroamino)-ethyl] Isocyanurate.
Polyesters. The polycondensation prods of dicarboxylic acids with dihydroxy alcohols. These cnpts may be modified by monocarboxylic acids or polyhydroxy alcohols. This definition includes the polycarbonates (qv), which are a well-defined segment of the general class of polyesters. Unsaturated polyesters, which are produced when any of the reactants contain non-aromatic unsaturation, can be cross-linked or copolymerized with an unsaturated copolymerizable monomer. The formulas and properties of the class "polyester" are as varied and extensive as the reactants themselves. For specific information on the various sub-classes and sub-sub classes, the following refs should be consulted: 9, 10, 11, 16a, 17, 18, 20, 23, 26, 29 & 38.

The ordn uses of polyesters are varied. They range from adhesives (Ref 4), amno boxes (Ref 5), grenade deactivator (Ref 7), component sealers (Refs 4 & 8), rocket launchers (Ref 1a), minesweeper hulls (Ref 14), to binders in exsPs (Refs 3, 6, 19, 21, 32, 33, 34, 35, 37 & 40), propints (Refs 12, 15, 16, 22, 24, 25, 27, 28, 30, 31, 32a, 32b & 39), and pyrots (Refs 2 & 13).

To illustrate the properties of exps with polyester binders, see the data in Table 1 from Refs 3, 6 and 37.

Bässer (Ref 19) developed a binder for extrusion-cast exps with the compn 70.0/19.0/7.3/3.7 bis(fluorodinitroethyl)-formal/epoxide B/maleic anhydride/diethylene glycol, using 0.5 wt % of ferric acetylacetonate as the catalyst. The binder is cured for 48 hrs at 60°. The cured binder has the following properties: d 1.487g/cc; DTA exotherms at 200° (minor) and 240° (major); a glass transition temp of −18°; thermal stability at 120°/22 hrs/0.25g sample evolved 0.76cc of gas (SITP).

Also in an invention of Frankel et al (Ref 40), a castable expl has been developed which, typically, consists of a polyester binder (20%) such as 3-(2',2'-dinitro-2'-fluoroethyl)-1,2-propadiol reacted with an isocyanate curing agent plus HMX (80%).

For other cnpts with polyester binders see the article on "Plastic-Bonded Explosives" in this Vol.

A current example of the use of a polyester resin as a propnt binder is the patd cnpt of Cohen and Scotoni (Ref 32b). In this formulation conventional polyester-olefinic copolymers are used (50.1) together with NG (42.5), triacetin (2.7), adiponitrile (2.7), PbO (0.5) and acetylsalicylic acid (1.5%) to obtain 27 and 152mm caseless ammo.

Exploratory work in the use of polyesters as pyrot binders was initiated at PA by Eppig in 1950 (Ref 2). He found that the Laminac series of resins, especially formulation 4116, which is an unsaturated polyester manufd by the American Cyanamid Corp (Ref 9), could be successfully used in a non-hygrosopic yellow flame ignition cnpt specifically developed for use with illuminant and signal cnpts contg Na nitrate. However, in a flare type cnpt contg Mg and Na nitrate together with Laminac 4116 polyester as the binder, Eppig found a marked decrease in burning time after one month storage at 65° (from 178 to 102 secs in one case). Because of this he recommended the use of a mercaptan resin binder (Thiokol) in flare cnpts. More recently, work by Haas (Ref 13) has shown that burning time is controlled by the length of the time expended in going from the
Table 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB49-3 (Ref 3)</td>
</tr>
<tr>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>RDX, %</td>
<td>60</td>
</tr>
<tr>
<td>HMX, %</td>
<td></td>
</tr>
<tr>
<td>Al, %</td>
<td>23</td>
</tr>
<tr>
<td>Polyester Resin, %</td>
<td>17</td>
</tr>
<tr>
<td>Paraffin wax, %</td>
<td></td>
</tr>
<tr>
<td>Cast density, g/cc</td>
<td>1.61</td>
</tr>
<tr>
<td>Detonation rate, m/sec</td>
<td>5855</td>
</tr>
<tr>
<td>Explosion Temp, °C</td>
<td>265</td>
</tr>
<tr>
<td>Impact Sensitivity:</td>
<td></td>
</tr>
<tr>
<td>a) PA App, 2kg, inches (TNT=14–15)</td>
<td>18</td>
</tr>
<tr>
<td>b) B/M Test, 221 lbs, feet, 50% pt;</td>
<td>no deton at 20ft</td>
</tr>
<tr>
<td>(TNT=11.2)</td>
<td></td>
</tr>
<tr>
<td>Max brisance, gm</td>
<td>58.7</td>
</tr>
<tr>
<td>sand crushed</td>
<td></td>
</tr>
<tr>
<td>Min detonation charge:</td>
<td></td>
</tr>
<tr>
<td>a) Tetryl, g</td>
<td></td>
</tr>
<tr>
<td>b) LA, g</td>
<td></td>
</tr>
<tr>
<td>Pendulum Friction</td>
<td></td>
</tr>
<tr>
<td>Rifle Bullet Impact:</td>
<td></td>
</tr>
<tr>
<td>a) Unconfined</td>
<td>5/5</td>
</tr>
<tr>
<td>no trials/unaffected</td>
<td></td>
</tr>
<tr>
<td>b) Confined</td>
<td>5/5</td>
</tr>
<tr>
<td>no trials/unaffected</td>
<td></td>
</tr>
<tr>
<td>no trials/partial deton</td>
<td></td>
</tr>
<tr>
<td>Vacuum Stability, 100°C, ml</td>
<td>0.32</td>
</tr>
<tr>
<td>gas/40 hrs</td>
<td></td>
</tr>
</tbody>
</table>

mixing to the pressing of a flare compn in which a polyester binder (the same Laminac 4116) is used. The shorter this manipulation time, the less the effect on burning time and other performance parameters. For addnl information and refs on Laminac 4116 see under this title in Vol 7, L3-L

Special Grenade”, PATR 2091 (1955)
9) J. Bjorksten et al., “Polymers and Their Applications”, Reinhold, NY (1956)
13) D. Haas et al., “Binding Properties and Other Characteristics of Several Polyester Resin Binders Used in Pyrotechnic Formulations”, Rept No RDTR No 51, USNAD, Crane (1966)
13a) V.V. Korsak et al., “Polymers—Lates”, (USSR), JPRS 33,612, TT: 66-30056 (1966)
22) G.W. Batchelder & G.A. Zimmerman, “Smokeless Propellant Compositions Containing a Metal Nitrite Burning Rate Catalyst”, USP 3653994 (1972) & CA 77, 77449 (1972)
24) G.W. Batchelder & G.A. Zimmerman, “Propellant Compositions Containing a Metal Nitrite Burning Rate Catalyst”, USP 3653994 (1972) & CA 77, 77449 (1972)
27) D.V. Sickman et al, “Propellant Composition with Crosslinked Binders Containing Nitro or Fluorodinitromethyl Groups”, USP 3745076 (1973) & CA 79, 94198 (1973)
37) A. Reichel et al, “High-Explo-
Polyether. A polymer in which the repeating unit includes a carbon-oxygen bond derived from aldehydes, epoxides, polycaprolactones or similar materials (Refs 1 & 4a).

Specific ordn using polyethers, such as Polyacrylate and Polyurethane, are entered separately below. Polymers already entered include Polymaleimide in Vol 6, F164-L to F167-L, and Epoxy Resins in Vol 5, E106-R to E107-L.

Some physical properties of model polyethers are presented in tabular form below (Ref 2).

Among the more than several uses for polyethers in ordn application is as a binder for extrusion-cast expls (Ref 3), and in a caseless propellant charge where the charge is used as an ammo element (Ref 5). Also, some development work on the use of Polyurethane resins (polyformaldehyde) as a fuel has been done by Singhal & T'ien (Ref 7).

Refs: 1) Beil - not found 1a) O. Schmidt & E. Meyer, “Ethers of Polyhydric Alcohols”, USP 1922459 (1933) & CA 27, 5082 (1933) 2) T.P. Hobin, “Model Polymers V - Some

<table>
<thead>
<tr>
<th>y</th>
<th>x</th>
<th>MP, °C</th>
<th>Density g/cc@20°</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>−95</td>
<td>0.982</td>
<td>1.420–1.440</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>−38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>−39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>−17.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>−69.9</td>
<td>0.966</td>
<td>1.445</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>−32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>−12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>−1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>−41.5</td>
<td>0.939</td>
<td>1.420–1.450</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>−5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>20.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>15.7</td>
<td>0.892(60°)</td>
<td>1.435–1.447</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Polyethylene Glycols. See in Vol 6, E252-L to E253-R under “Ethylene glycol Polymers; Polyethylene glycols or Polyglycols”.


Polyethylene glycol ethers. These comps are recommended as adms to gelatin Dynamite in quantities of about 0.4% to improve plasticity. They usually contain at least 8 linear carbon atoms and at least two adjacent ethyleneoxy groups

Ref: S. Fordham & J.L. Moilliet, BritP 586224 (1947) & CA 41, 7120 (1947)


Polyethylene Peroxide. See under “Ethylene peroxide, Polymeric” in Vol 6, E306-R

Polyethyl Methacrylate. See under “Ethyl Methacrylate” in Vol 6, E308

Polyfunctional Organic Azides

An improvement in M2 proplnt is offered by the work of Kuhn and Duckworth of BRL (Ref 2). By incorporating independently several diazidodinitrates; viz, 2,3-Diazido-1,4-Dinitrobutane and 3,3-Diazido-2,4-Dinitrotetramethane, they obtd proplnt films that compare favorably with M2 proplnt but have lower flame temps (see tabulated data below). See also “Organic Azides” in Vol 1, A627-R to A644-L and diazidos in Vol 5, under various diazidocomps, D1154-R to D1155-R

2,3-Diazido-1,4-Dinitrotobutane (DADNB).

(NO3)2CH2.CHN3.CHN3.CH2(NO3); mw 262.21; N 42.74%; OB to CO2 −30.51%; cryst (meso), liq (racemic); mp 70–71°C (cryst); bp 150°C (decompr). Sol in acet and ethanol. Prepn is by nitration of 2,3-diazido-1,4-butanediol with mixed acid. The procedure involves dropwise addn of 2.58g of the diol to a cooled (0–5°C) mixt (1/1) of acetic anhydride/100% nitric acid. The reaction is held to 5–15°C and stirred for 30 mins. Several recryst from ethanol give a (approx) 40% yield. The compd is friction sensitive; Qc 682.8 and 671.8 kcal/mole; Qf 98.8 kcal/mole; impact sens at 50% pt is 6.3 cm using a 2kg wt in an Aberdeen Impact App and No 12 tools (PETN=26.7 cm); impact sens of proplnt films (85.15% NC/14.85% diazido compd) is 29–36 cm (M2 film=34–36 cm) at the 50% pt

3,3-Diazido-2,4-Dinitrotetramethane (or DADNPE).

CH3.C.C(N3)2.CH.CH3;

ONO2 ONO2

mw 276.24; N 40.63%; OB to CO2 −46.34%; mp 64–66°C; bp 135°C (decompr); sol in ethanol & hexane. Prepn is by slow dropwise addn of 4.2g of 3,3-diazido-2,4-pentanediol to a cold (0–5°C) mixt of (1/1 molar) acetic anhydride/100% nitric acid. The temp is maind at 5–15°C for 30 mins while the mixt is stirred. Several recryst from hexane give an 85% yield. Compd is friction sensitive, expln temp is 165°C; Qc 828.0, 822.8 kcal/mole; Qf 85.4 kcal/mole; impact sens at the 50% pt is 5.7 cm using a 2kg wt in an Aberdeen Impact App with bare No 12 tools (PETN=26.7 cm); impact sens for proplnt film (78% NC/22% diazido compds) is 29–36 cm (M2 film=34–36 cm) at the 50% pt

Calc the using TIGER code of the parameters of M2 proplnt compn using each of the diazido compds vs NG or HMX is presented in Table 1
Table 1
Calculated Properties of M2 Propellant Substituting the Diazido Compounds for Compound X

<table>
<thead>
<tr>
<th>Property</th>
<th>Compound X Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition:</td>
<td>T, °K Force, in-lbs/lb Pc psi</td>
</tr>
<tr>
<td>NC (13.15% N)</td>
<td>3410 4.52x10^6 39600</td>
</tr>
<tr>
<td>Ethyl Centralite,</td>
<td>3270 4.65x10^6 40500</td>
</tr>
<tr>
<td>Water,</td>
<td>3120 4.46x10^6 39800</td>
</tr>
<tr>
<td>Graphite,</td>
<td>3230 4.48x10^6 39600</td>
</tr>
<tr>
<td>Ethanol,</td>
<td></td>
</tr>
<tr>
<td>Compound X,</td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td></td>
</tr>
<tr>
<td>DADNBX</td>
<td></td>
</tr>
<tr>
<td>DADNPE</td>
<td></td>
</tr>
<tr>
<td>HMX</td>
<td></td>
</tr>
</tbody>
</table>

Refs: 1) Beil – DADNBX not found & DADNPE not found  2) L.P. Kuhn & A.C. Duckworth, “The Preparation of Some New Polyfunctional Organic Azides”, BRL Rept No 1607 (1972); also, the following limited distribution Addnl Ref: Y.P. Carignan, “Evaluation of Some New Polyfunctional Organic Azides for Propellant Applications”, PATR 4592 (1973)

Polygalitol and Polygalitol Tetranitrate.
1,5-Anhydro-d-Sorbitol (3,4,5,1-Tetraoxy-1-methyl-pyranotetrahydrate, Polygalitol or Galgit (Ger).

\[
\text{HO.CH}_2 \text{C} = \text{C} - \text{C} - \text{C} - \text{CH}_2 \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{O}
\]

Colorless prisms or ndles (from ethanol); mw 164.205; mp 142–43°; bp, decomps on distn. V sol in ethanol; v sl sol in acet acid. Prepn is by prolonged heating of tannin with a 5%aq sulfuric acid soln. It is also a coprod of the hydrogenation of tetraacyt-2-oxy-glucal (Ger) with a Pd catalyst followed by saponification with Ba hydroxide

Ref: Beil 17, 191 & [235]

Polygalitol Tetranitrate. OC\textsubscript{6}H\textsubscript{4}(ON\textsubscript{2})\textsubscript{4}; mw 344.25; N 16.28%; OB to CO\textsubscript{2} -13.94%; ndles (from ethanol), prisms (from chlif); mp 106°. V sol in acet, benz, eth and acet acid; v sl sol in cold ethanol; sl sol in hot ethanol; insol in w.

Prepn is by reacting 5g of galitol with 50cc of cold mixed acid (sulfuric and fuming nitric).
Polygalitol tetranitrate expls under heavy impact
Ref: Beil 17, 191

Polyglycidyl 2,2-Dinitro-2-Fluoroethyl Ether Binder for Explosives.

Monomer: Glycidyl-2,2-Dinitro-2-Fluoroethyl Ether (2,3-Propane epoxide-2,2-Dinitro-2-Fluoroethyl Ether).

\[
\text{H} \quad \text{H} \\
\text{HC} - \text{C} - \text{CH}_2 \cdot \text{O} - \text{CH}_2 \cdot \text{C} (\text{NO}_2) \text{O}_2 \cdot \text{F} \\
\text{O}
\]

mw 210.15; N 13.33%. Prepn is by oxidn of 2,2-dinitro-2-fluoroethyl alkyl ether with peroxyl trifluoracetate, hydrogen peroxide and (CS\textsubscript{2}CO\textsubscript{2})\text{O}. Yield is 58%

Polymer: Polyglycidyl 2,2-Dinitro-2-Fluoroethyl Ether.

\[
\left[ \text{H}_2 \text{C} . \text{CH}_2 \cdot \text{O} - \text{CH}_2 \cdot \text{C} (\text{NO}_2) \text{O}_2 \cdot \text{F} \right]^n
\]

mw 784–2660; OB to CO\textsubscript{2} -87.56%. Quant polymerization occurs in the presence of BF\textsubscript{3} etherate catalyst. A typical expn compn consists of 80% RDX and 20% polymer. Expl power for compn is 1667 (RDX=1859; RDX/polybutadiene=1017)


Polyglycidyl Nitrate (Polyurethane) Propellants (PGN). A series of propln comps developed by both JPL of Cal Tech and the Aerojet-General Corp in the late 1950’ (Refs 2 & 3), using as the binder fuel a polyurethane resin prepd from PGN. JPL used either Amm Nitrate or Amm Perchlorate as the oxidizer (Ref 2), while Aerojet used Amm Perchlorate with plasticizers such as 4-Nitrazapentanoniotine (NPN) and 2,2-Pentanoate (TNENP) in a plasticizer-to-binder wt ratio of 0.6 (Ref 3).

Since Glycidyl Nitrate is the monomer of PGN, its properties should be noted in Vol 6, G110-R under Glycidy Nitrate

Polyglycidyl Nitrate (PGN)

\[
\left[ \text{H}_2 \text{C} - \text{C} - \text{C} (\text{NO}_2) \right]^n
\]
Polyhydric Alcohols. (Polyols). An alcohol with three or more hydroxyl groups, each attached to a different carbon atom. They are w-sol and of sweetish taste, which tends to intensify with increasing hydroxyl content. Examples of polyols of ordn interest are listed below. Polyvinyl alcohol is considered in a separate entry as a polymer although it is defined as a polyhydric alcohol. Polyols, when nitrated, make excellent epox, propellant binders, plasticizers, etc. Prepn can follow the procedure of Lenth & DuPuis (Ref 3) which uses a methanol suspension of either sucrose or dextrose and a special Cu-Al oxide catalyst to yield 60–65% distillable polyols at 240°F and 1500psi.


Polyglycol ethers. See “Glycol, Monophenyl-ether of” and “Glycol, Tertiary ethers of” in Vol 6, G116

Polyglycols. See “Ethylenglycol Polymers, Nitrated” in Vol 6, E279-R.
proplnt plasticizers, or as utilized in other ancillary functions germane to ammo are presented below:

**Butanetriol and Derivatives.** See Vol 2, B370-R to B371-R

**iso-Butanetriol and Derivatives.** See Vol 2, B371-R to B372-R

**D-sorbitol and Derivatives.** See Vol 3, D91-R to D92-L

**Diglycerol and Derivatives.** See Vol 5, D1261-L to D1262-L

**Dipentaerythritol and Derivatives.** See Vol 5, D1407-L to D1413-L

**Dulcitol and Derivatives.** See Vol 5, D1567-R to D1568-L

**Erythritol (and Derivatives).** See Vol 5, E123-L to E125-L

**Glucose and Derivatives.** See Vol 6, G83-R to G84-R

**Glycerol or Glycerin and Derivatives.** See Vol 6, G87-R to G93-R

An addnl glycerol compd used as a propant binder is presented next

**Ethylene glycol-1,6-Dichloro-2,5-Diazahexane-Glycerol-Copolymer.** D 0.065lb/inch³. Prepn is by reacting 0.6 mole of 1,6-dichloro-2,5-dinitro-2,5-diazahexane with 0.56 mole of ethylene glycol and 0.11 mole glycerol by stirring for 24 hrs at 50–60° under partial vac. The copolymer formed (19.2) is combined with Al (12.0), HMX (65) and hexamethylene diisocyanate (3.8%) to form a propant with a burning rate of 0.21inch/sec at 1000psi, and a sp im-

pulse of 265


**Hydrocellulose.** See Vol 7, H213

**Mannitol and Derivatives.** See Vol 8, M13-L to M16-R

**Methyl Glycoside and Its Tetranitrate.** See Vol 8, M106

**Methyl Trimethylolmethane and Derivatives.** See Vol 8, M116-R to M118-L

**Metriol and Its Derivatives.** See Vol 8, M120-R to M122-L

**Pentaerythritol and Its Derivatives.** See Vol 8 (qv)

**Phloroglucinol and Its Derivatives.** See Vol 8 (qv)

**Polyvinyl Alcohol and Its Derivatives.** See Vol 8 (qv)

**Poly hydrogen Cyanide (Azulnic Acid).** Anhydrous HCN is stable at or below RT (See Vol 2, C167-L under AC) if inhibited with 0.1% sulfuric acid. However, in the absence of inhibitor exothermic polymerization occurs. At 175°, explosively rapid polymerization occurs after an induction period of 27 mns. If the temp reaches 184°, explosively rapid polymerization occurs immediately. A trace of alkali (2x10⁻⁵ mole NaOH/g HCN) at 100° induces expl polymerization in 304 mns. If a trace of w is present at RT, ammonia is released from the HCN, which polymerizes autocatalytically producing a modified polymer. Polymerization is accelerated by any matl capable of accepting a
proton from HCN, such as metallic hydroxides, cyanides, cyanates, ammonia, tertiary amines and baked Vycor glass. Acceleration also results from any energy input that ionizes the HCN, such as ultraviolet light in aqueous solution and ionizing radiation in both the liquid and gas phases. Indeed, tritium cyanide polymerizes rapidly because of self-radioysis (Ref 7). The Q_poly is 377 cal/g (Ref 2).

A lab procedure reported in Ref 7 yields an almost theoretical compn of (HCN)_x. Liq HCN dild with an equal wt of chl is polymerized by reacting with 5 wt % of tributylamine for eight hrs at 25°C in the absence of w and air. The polymer produced is comprised of several comps. The simplest is the tetramer of Diaminomalonitrile, (HCN)_4; lab yield is 15%; mp 184°C (decomp). Sol in boiling w. A much more complicated, w insol, cryst material is also produced.

The polymer, mixed with cyanogen, has been proposed for use as a rocket fuel (Ref 7).

Polymeric Peroxides. See under "Peroxides" in this Vol

Polymerization, Violent. Violent monomer polymerization has caused a number of serious expns. Present in Table 1 below is a summary of data pertinent to the causation of these expns, extracted from the ref. The monomers listed may be found under appropriate entry titles throughout the Encycl.

Polymerized Acetaldehyde. See Vol 1, A14-L to A15-L under "Formaldehyde..."

Polymerized Alcohols. Polyhydric alcohols (qv) such as pentaerythritol, sorbitol and glyceral can be used as the polyol component of polyethers (qv) which are used as expl and propellant binders. Polyhydroxypropylene derivs of sorbitol have been employed extensively as components of polyurethane resins (qv), also employed as a propellant binder.
Ref: J.A. Monick, "Alcohols - Their Chemistry, Properties and Manufacture", Reinhold, NY (1968), 414

Polymerized Allyl Type Alcohols. See Vol 1, A135-R to A136-L. A patented process (Ref) obtains polymers by heating allyl alc, or homologs, at 50-100°C in the presence of oxygen and/or an oxygen-yielding catalyst such as a peroxide, perchlorate or persulfate. Nitration of these polymers has yielded some expns.
Ref: Anon, Dutch P 66784 (1950) & CA 45, 5451 (1951)

Polymerized Formic Aldehyde. See Vol 6, F164-L to F165-L under "Formaldehyde Polymers"

Polymerized Glycerin. A prod first obtd by Wohl (Ref 1) by heating glycerin to 130-60°C with a small quan of sulfuric acid. The viscous prod contained glycerin (30-40%), diglycerin (54-66%), and polyglycerin (4-6%), becoming an oil on nitratation (Ref 3). Will and Störer (Ref 2) improved the process by boiling glycerin at 290-95°C for 7-8 hrs with only the addn of about 0.5% soda or alkali sulfides. The yield is 60% diglycerin which can be vac distd from the prod mixt and nitrated to the expl tetranitrate (Ref 4). See also "Diglycerol and Derivatives" in Vol 5, D1261-L to D1262-L.
Ref: 1) A. Wohl, GerP 58957 (1890) 2) Will & D. Störer, SS 1, 231 (1906) 3) P. Naoum, "Nitroglycerin", Williams & Wilkins, Baltimore (1928), 199 4) Urbaniński 2 (1965), 138-40
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
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**TABLE 1**

A Summary of Data Pertinent to Violent Polymerization
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<td>Acute toxicity</td>
<td>Oral: LD₅₀ = 3000 mg/kg</td>
<td>Acute toxicity</td>
<td>Oral: LD₅₀ = 4000 mg/kg</td>
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<td>Skin: ID₅₀ = 1000 mg/m²/day</td>
<td>Chronic toxicity</td>
<td>Skin: ID₅₀ = 1500 mg/m²/day</td>
<td>Chronic toxicity</td>
<td>Skin: ID₅₀ = 2000 mg/m²/day</td>
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<td>Non-combustible</td>
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<td>Non-combustible</td>
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<td>Non-oxidizing</td>
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<td>Solubility</td>
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<td>Soluble in water and ethanol</td>
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<td>Reactivity</td>
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</tbody>
</table>

**TABLE 1 (Continued)**
Polymers, Explosive. See under individual names. Generally, explosive polymers are synthetic substances composed mainly of low mw molecules containing explxorophores such as peroxide linkages, nitro, nitrate, azo groups, etc (see under “AUXOEXPLOSE...” in Vol 1, A513-L to A514-R). The nomenclature used is identical to that used for non-exp explomers; viz, expl polymers are approx multiples of low mw units called monomers. An expl compd of higher mw is produced in a process called polymerization. The polymer so produced may have combined several varieties of both expl and non-exp monomers such as organic acids and alcohols. When only two monomers of any type are used, the resulting compd is called a copolymer; if three varieties, terpolymer, etc. Examples of expl polymers can be found under “NITOPOLYMER” in this Vol, N138-R ff, Polyglycidyl Nitrate (qv), and Petrin Acrylate (qv) Ref. 1) Urbanski 1 (1964), 1-5

Polymers of Dextrose. See in Vol 5, D1116

Polymethylmethacrylate (Lucite, Plexiglas, Crystalline or PMMA). A thermoplastic translucent resin of the acrylate resin family. The monomer, methyl methacrylate;

\[
\begin{bmatrix}
\text{O} \\
\text{H C O CH}_3 \\
\text{C C} \\
\text{H CH}_3
\end{bmatrix}
\]

are as follows: mw approx 1x10^6; OB to CO₂ -191.79%; optically clear atactic or predominantly syndiotactic solid; softening pt 130°C; d 1.18g/cc; RI 1.49. Sol in acct, ethacetate, ethylene dichloride, carbon tetrachloride, toluene, acetic acid, and formic acid; insol in w, and many aq inorganic reagents at RT such as hydrochloric acid or amm hydroxide (Refs 2a, 3 & 6a).

Prepn by emulsion polymerization, according to Resnick (Ref 3), is as follows: “A 5-liter 3-neck flask is used. The center neck is fitted with a mercury-sealed stirrer having a sidearm gas inlet. One side neck carries a standard-taper thermometer and the other a “Y” tube, one arm for a condenser and the other for taking samples. Two kg of distilled water is placed in the flask, and the water is brought to a boil by means of a Glas-Col mantle. The mantle is removed and the water allowed to cool to room temperature under an atmosphere of nitrogen. Making certain there is a positive nitrogen pressure in the flask, it is then opened and 10 grams of “Duponom” ME (an emulsifier), 1 gram of K₂S₂O₅, and 1 kg of methyl methacrylate containing 1 gram of dodecyl mercaptan is added in that order. With good stirring the flask is then heated at 40–42°C. Samples of about 5ml of latex are withdrawn periodically by pipette, and the total solids determined by drying under infra-red. At the end of 2.5 hours the yield should be 88%. At that point the reaction is stopped by shutting off the nitrogen, cooling the flask to ambient temperature, and adding hydroquinone. To precipitate the polymer from the latex, the latex (one volume) is added drop by drop to 3 volumes of ethanol with rapid stirring. About 1/3 volume of water (based on ethanol) is then added and stirring continued for 5 minutes. The mixture is placed on a steam bath, warmed to 45–48°C, and then allowed to stand until the polymer is completely coagulated. The polymer is filtered, and washed with a 70/30 mixture of ethanol and water by stirring for 15 minutes. After being filtered again, the polymer is washed 4 times with 1-liter portions of water,
with a filtering after each washing. The poly-
methyl methacrylate is then placed in glass
trays and dried at 58°C for 18 hours. The dried
polymer is crushed down and re-dried at 53°C
under vacuum for 7 hours”.

Methyl methacrylate can also be polymerized
by radiation using either a cobalt-60 source or
accelerated electrons at dose rates up to 3
megarads/sec. The activation energy for the
electron beam polymerization is about 7.0 kcal/
mole (Ref 12). Radical polymerization can also
occur using diisocyanates or hydroperoxides
as the initiating species (Ref 15).

Block copolymers with materials such as a
polyester (PE) (qv) can be prepared by the reaction
of diisocyanate-terminated polyesters with hy-
droxyl-terminated PMMA according to Wilkes
and Grezlak (Ref 21). The basic structure was
found to be PMMA-PE-PMMA, with a mw of
from 7500 to 47000. The purpose of the work
was to produce a stronger copolymer (in terms
of stress-strain) by tailoring the amt of each
monomer used to produce the copolymer

Further information on polymerization can be
found in Refs 2a & 6a

PMMA finds ordn usage in several areas:
in ballistic or impact shields for missiles or air-
planes; also as windows, windshields or canopies
in aircraft (Refs 7 and 22); as a Laser Q switch
host using an organic Ni complex dye (Ref 22);
and in propelants as fuel (with Al and NG as co-
fuels — Ref 20) and Amm perchlorate or K
 perchlorate as oxidizers (Refs 2, 4, 8–11, 13,14
 & 16–20). Also see under “Aeropex Propell-
ants” in Vol 1, A108-R and under “Composite
Propellants” in Vol 3, C464-L to C474-L

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(1975) & CA 83, 118018 (1975) 20) V.S.
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Polynitramides. Several compds of the type \( \text{C}_n \text{H}_{11} \left[ \text{NNO}_2 \text{CH}_2 \text{CH}_2 \right]_n \text{NNO}_2 \text{C}_6 \text{H}_{11} \), where \( n = 1 \) to 4, were prepped and examined by Harpham et al (Ref 1). These dicyclohexyloxyethylene-polynitramides are high melting (171.5° avg) highly insol solids, exceptionally difficult to detonate, which do not respond to the Gránchimort test for the nitramino group.

Other polynitramides have been synthesized by Frankel and Klager (Ref 2). These compds are of the type \( \text{RC(O)NHCH}_2 \left[ \text{AN(NO}_2 \right]_n \text{CH}_2 \text{A'NH(C(O)R'} \), where \( R \) and \( R' \) are alkyl radicals, \( A \) and \( A' \) are alkylene radicals, and \( n = 1 \) to 4. Their prepn consists of condensing the appropriate polynitrodiamines derived from nitrazadisocyanates and strong mineral acids with acid anhydrides. These compds are considered by their inventors to be suitable for use as the main exp charge in shells, missiles and blasting charges, or as O donors and modifiers for propf fuels. To date, little ordn use has been found for them.

For more information on “Nitramides”, see this entry in this Vol, N28-R to N29-L

Polynitroamines. A series of compds developed by Frankel and Klager (Ref 3) as expts and O donors in propf fuels. These compds are preped by condensing \( \beta \)-geminal polynitro alcohols with ammonia or polynitro amines. The compds produced are of the type, \( \text{RC(NO}_2 \right]_2 \left( \text{CH}_2 \right)_{n} \text{NH(CH}_2 \right]_x \text{C(NO}_2 \right]_3 \); and yield Pb block values of approx 140 (TNT=100) and Ballistic Mortar values of approx 140 (TNT=100). See also “Amines, Nitrate and Nitrited” in Vol 1, A174-R to A177-R


Polynitrodiphenylmethanes. See “Diphenylmethane and Derivatives” in Vol 5, D1464-L to D1466-L. Hexanitrodiphenylmethane had not been synthesized as of 1966. However, since then the work of Shipp and Kaplan (Ref 2) in 1976 allows the following entry to be made: 2,2',4,4',6,6'-Hexanitrodiphenylmethane.

\[
\begin{align*}
\text{NO}_2 & - \text{CH}_2 - \text{NO}_2 \\
\text{O}_2 \text{N} & - \text{NO}_2 - \text{O}_2 \text{N} - \text{NO}_2
\end{align*}
\]

mw 438.24; N 19.18%, OB to CO\(_2\) − 62.07%. Prepn is by treating TNT in tetrahydrofuran with a mix of methanol-KOH, and then with picryl chloride in the presence of Me\(_2\)SO. The prod of this step is then oxidized with chromic oxide in a nitric acid–oleum mixt to yield the polynitrodiphenyl methane. The compd is expl


Polypropylene. The lowest density homoplastic obdt by stereoselective catalysts

Monomer

Propylene (Propene). \( \text{CH}_3\text{CH}:\text{CH}_2 \); mw 42.08; colorl gas; mp −185.25°, bp −47.4°, d 0.5193 at 20/4° (liq at atm press); R1 1.3567 at −40°. V sol in acetic acid, ethanol and w. Prepn is by dehydrozation of propen-2-ol over Al oxide at 330°. It is also obdt as a pyrolysis product of propane and as a fraction of petr well head gases. Prepn has a \( Q_c \) of 460.47 kcal/mole; the expIn limits with air are 2.0 to 11.1% (Ref 2); it has an autoign temp of 927°F. Under unusual conditions, such as 955 atm press and
327°, propene has been known to expld (Ref 5a) 

Propene is a simple asphyxiant. Rapid evap 
from the liq can cause skin burns due to its 
refrigerant effect on tissue 

For the “Propenes and Derivatives” of ordn 
interest, see under that title in this Vol 
Polymer 

Polypropylene was first produced commercially 
in Italy and called “Moplene” (Ref 2), 

![Polypropylene chain](image)

(C₃H₆)₇, mw > 40,000; crystn wh powdr; 
mp 165–70° (isotactic); d 0.90–0.91g/cc; 
max breaking strength 300–50kg/cm²; impact 
strength (extension) 80kg/cm², (compression) 600–700kg/cm²; max useable temp is 
150°. Sol in aromatic hydrocarbons such as 
benz or toluene at temps > 80°; insol in all 
organic solvents at RT. Prepn is by the use of 
Ziegler-type catalysts at an optimum temp of 
120° (Refs 2 & 3). The polymerization is ac-
complished using a mixt of 30/70 (liq) propy-
lene/propane or pure propylene dissolved in 
n-heptane with an Al alkyl (trisobutyl or tri-
hexyl) titanous chloride catalyst (Ref 2) 

Polypropylene (film) has a Q_c of 11074.5 
cal/g (Ref 5) 

The ordn uses for polypropylene are varied. 
It is used in the fabricration of personnel body 
armor (Refs 6 & 7); in slurry-explos for the 
demolition of concrete structures (Ref 11); as 
a microporous hydrazine-air (cathode) separator 
in fuel cells (Ref 9); as a propiite binder mtrl, 
particularly in caseless ammo, (Refs 5 & 8); 
and as a candidate to act as a propiite aging 
inhibitor for the 155mm RAP round (Ref 10) 
Refs: 1) Bell 1, 196, (82), [167], (677) and 
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and Biconstituent Fibers in Ballistic Fabric for 
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Propellant Grains of 155mm HE RAP (Rocket 
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75, Contract DAAA21-75-C-0267, NY Univ, 
NY (1975) 11) T. Takayama, JapP 7518052 
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Rub Hdbk (1975), C-457 

Polynitrostilbenes. See under “Nitrostilbene” 
thru “... HNS...” in Vol 5, D1454-L thru 
D1457-R, and under HNS in Vol 7, H162-L 

Polystyrene. A thermoplastic used as a binder 
and fuel in exps and rocket proplnts. See 
“Plastic fuels” (Vol 3, C465-L) under “Com-
posite Propellants”; also “Dinitropolystyrene” 
in this Vol, N143-L to N144-R under “Nitro 
Polymers”; and “Propellants, Solid”, also in 
this Vol
Polysulfide Polymers. These polymers are made up of aliphatic hydrocarbon units connected by di-, tri- or tetradsulfide links. The synthetic rubber found useful in ordn has hydrocarbon units linked by either O or formal segments. The polymers are usually prep'd by the condensation of a suitable organic dihalide, usually the chloride, with aq Na polysulfide. According to Ref 8, the most practical organic dichloride is dichlorodiethylformaldehyde; viz., Bis[2-chlor-ethoxy]-methane (Dichlorodiethylformal or Formaldehyde-[bis-(2-chlor-ethyl)-acetall]); CH₂ClCH₂.OC₂H₄.CH₂.Cl, mw 173.06; liq; bp 218.1°, d 1.2339g/cc; RI 1.4540. Sol in and forms an azoetropic with w. Prep is by treating a mixt of paraformaldehyde and 2-chloroethanol with aq HCl (Ref 1).  

Liquid Polysulfide (Pre) polymer.  
HS-[C₂H₄.O.CH₂.OC₂H₄.SS]₉C₂.H₄.O.CH₂.O.C₂SH; mw (range of avg) 500 to 7500; mobile amber liq; d 1.27 to 1.31g/cc. Sol in a wide variety of solvents such as alcohols, ethers, ketones, etc. Prep is by treating dichlorodiethylformal with Na polysulfide (Refs 2, 3, 4 & 8). The Thiokol LP-3 (Thiokol Chem Corp) version of the liq polymer is prep'd by the reaction of 98 mole % dichlorodiethylformal and 2 mole % trichloropropane with an excess of Na polysulfide. The aq layer is treated with Na hydrosulfide and Na sulfite, bringing about a controlled cleavage of the high mw polymers to liq prepolymer of low mw (Ref 15). For information on Thiokol Propellants see "Composite Propellants" in Vol 3, C467-L and "Propellants, Solid" in this Vol. The liq prepolymer ignites upon contact with dry Ca peroxide (Ref 11). Open cup fire pt is 465°F and flash pt is 418°F (Thiokol LP-3, Ref 10)

The liq prepolymer are cured or polymerized by heating them with oxides or peroxides such as ZnO, Zn peroxide, PbO, or p-quinone dioxime. A high mw crystal polymer is produced which has a useful temp range of -65° to 350°F, an outstanding resistance to swelling in oils and solvents such as carbon tetrachloride, and an impermeability to vapors, gases, ozone, oxygen and light (Ref 4).

By far the greatest ordn application for polysulfide polymers is in Thiokol propellants (Refs 1, 2, 4, 5, 8, 14 & 15). However, other applications exist, ie, in expls (Refs 9 & 16), in other types of propellants (Ref 12), and in pyrots (Thiokol LP-2, Ref 13).

The US Mil Spec covering liq polysulfide polymers for use in the 3.0-inch, Mark 32 Mod 0 Rocket Motor, MIL-P-23702 (WEP), 10 May 1963 contains the following requirements and criteria (Tables 1 and 2).

**Table 1**  
**Chemical Requirements**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercaptan (as SH), % a</td>
<td>5.0 - 6.5</td>
</tr>
<tr>
<td>Moisture, % b</td>
<td>- 0.1</td>
</tr>
<tr>
<td>Acidity (of w extract), pH c</td>
<td>5.8 - 8.9</td>
</tr>
</tbody>
</table>

a — By iodometric titration  
b — By absorption of the w using dry toluene from the polymer followed by dist of the toluene plus w into a cold finger moisture measurement trap  
c — By electrometric detn of pH
Table 2
Physical Requirements for the Liquid Polymer
and Cured Compounded Test Sheets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
</tr>
<tr>
<td>Viscosity of Liq Polymer, Cps a</td>
<td>1300</td>
</tr>
<tr>
<td>Tensile Strength, psi b</td>
<td>350</td>
</tr>
<tr>
<td>Tensile Stress at 500% elongation, psi c</td>
<td>200</td>
</tr>
<tr>
<td>Ultimate Elongation, % d</td>
<td>800</td>
</tr>
<tr>
<td>Hardness, Shore A e</td>
<td>32</td>
</tr>
</tbody>
</table>

a – By means of a Brookfield Helipath, Model RFV viscometer at 80°F (Brookfield Engng Co., Stoughton, Mass)
b – By means of an Instron testing machine
c – Ibid
d – Ibid and calcn
e – By means of a Shore Durometer, Type A, or approved equivalent

In addition to the above, Qualification Tests are required consisting of acceptable performance when incorporated with other satisfactory materials in a test batch of N-26 Propellant Composite (Spec MIL-P-23735 (WEP)).


Polytetrafluoroethylene (Teflon, PTFE, Fluon, Fluoroflex, Polytef, TFE). A thermoplastic homopolymer composed of long chains of —CF₂— units. Colorless to grey powder, flakes or grains. Grayish white transparent thin sheets. Useful temp range –75° to 250°. Gels at 235° and at 400° reverts to the gaseous monomer. D 2.25g/cc; Shore hardness 55–56; tensile strength 3500–4500psi; flexural strength 2000psi; brittle pt below –80°; dielectric const (at 60 to 3x10⁹ cycles) 2.0–2.05. Prep by polymerization of tetrafluoroethylene

Not affected by w, aqua regia, chlorosulfonic acid, acetyl chloride, B fluoride, hot nitric acid, boiling solns of NaOH and organic solvents. Not wetted by w. No substance has been found which will dissolve the polymer, but prolonged contact with fluorine, hot plasticizers and polymeric waxes is not recommended (Refs 1 & 6)

In ord applications, powdered PTFE has been used primarily in pyrot and propellant areas. Infra-red pyrot flares have been based on pressed Mg/PTFE formulations since the 1950's (Ref 3). Allen (Ref 2) obtained a high regression rate by supplementing the surface energy of the solid fuel compn of hybrid rocket motors with Mg/PTFE used at approx 10% by wt. Kaufman and Roy (Ref 4) used 2–10% PTFE powder in composite proplnt compns; during extrusion it was cold-drawn to form fibers which strengthened the product. Igniter compns contg 20–50% Mg powder, 20–30% small particle size PTFE and 10% silicone rubber have also been patented.
PTFE has also been used in some expl nuts, where a PTFE insert provides a self-locking feature of the thread and a gas-tight seal between thread segments, bolt and housing (Ref 5). It has also been used to make inert seals or containers for pyrot compns (Ref 1).

Powdered Teflon for use in pyrots is covered by US Mil Spec MIL-P-48296(PA) (1 May 1974), "Polytetrafluoroethylene (TFE)". Three classes of material are specified (1, 2 & 3). The requirements are: purity, 99.4% min; infrared spectrum, peaks consistent with figure shown; color, TFE shall be opaque and the color shall range from white to gray; moisture, 0.05% max; ash, 0.1% max; mp, 337°± 0°C; packing density, Class 1 – 1.18 ± 0.13g/cc, Class 2 – 1.25 ± 0.02g/cc, Class 3 – 1.14 ± 0.02g/cc; particle size by sieve analysis, Class 1 – 95 ± 15 microns, Class 2 – 237 ± 27 microns, Class 3 – 200 ± 30 microns; particle size distribution by sieve analysis, as specified in Table 1.

<table>
<thead>
<tr>
<th>US Standard Sieve Size</th>
<th>Percent Retained On</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1</td>
</tr>
<tr>
<td>40</td>
<td>–</td>
</tr>
<tr>
<td>50</td>
<td>–</td>
</tr>
<tr>
<td>60</td>
<td>0.8 max</td>
</tr>
<tr>
<td>70</td>
<td>–</td>
</tr>
<tr>
<td>80</td>
<td>–</td>
</tr>
<tr>
<td>100</td>
<td>5 max</td>
</tr>
<tr>
<td>120</td>
<td>11–29</td>
</tr>
<tr>
<td>140</td>
<td>15–26</td>
</tr>
<tr>
<td>170</td>
<td>11–21</td>
</tr>
<tr>
<td>200</td>
<td>7–16</td>
</tr>
<tr>
<td>325</td>
<td>9–25</td>
</tr>
<tr>
<td>Pan</td>
<td>9–26</td>
</tr>
</tbody>
</table>

Polythiocyanogen. (SCN)x: mw (58.08)x: N 24.12%; brick red solid; mp, decomp when heated over 300°. Insol in w and the usual organic solvents as well as weak acids and alkalies. Comm prep (Ref 3) is from thiocyanic acid and/or thiocyanates either by anodic oxidation or by interaction with hydrogen peroxide or halogens. The yield is impure because it contains both H and O. The S content varies between 45 and 55%. Lab prep of the pure polymer is by reacting the Na salt of 5-chloro-3-mercaptop-1,2,4-thiazoloz complete with either acet, ethanol or w (Refs 1 & 2).

Audrieth (Ref 3) patented the use of (SCN)x as a fuel in primers, ignition and fuze time trains (see Table below). A significant advantage of the invention for fuze time train usage over BlkPdr is the greater control evidenced in the rate of burning.

---

**Table 1**

Particle Size Distribution Requirements for TFE

Table 1
Examples of (SCN)_x Usage in Energetic Materials

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ordnance Applications, % of Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primers</td>
</tr>
<tr>
<td>(SCN)_x</td>
<td>10</td>
</tr>
<tr>
<td>K chlorate</td>
<td>51</td>
</tr>
<tr>
<td>Sb trisulfide</td>
<td>34</td>
</tr>
<tr>
<td>Pb azide</td>
<td>5</td>
</tr>
<tr>
<td>Ba peroxide</td>
<td>-</td>
</tr>
<tr>
<td>K nitrate</td>
<td>-</td>
</tr>
<tr>
<td>K perchlorate</td>
<td>-</td>
</tr>
</tbody>
</table>


Polyvinylacetate. A thermoplastic primarily used as a binder in non-metallic cartridge cases (see Mil Spec below)

Monomer
Vinyl Acetate. CH₃C(O).O.CH₂.CH₂; mw 86.09; colorless, mobile liq; mp -93.2⁰, -100.2⁰; bp 72.2⁰, 73⁰; d 0.9335g/cc; RI 1.3959. Sol in hot w, ethanol, eth, acet, benz, cH4. Prepn is by addn of acetic acid to acetylene in the vapor phase at 200⁰ over Zn or Cd acetate catalyst (Refs 1, 4, 6a & 7). Autoign temp 800⁰F; flash pt 18⁰F; expl limits (in air) are 2.6–13.4%. Exposure of vinyl acetate to light produces the polymer (Ref 2a)

Polyvinylacetate. (C₂H₄O₂)ₓ where
\[
\begin{align*}
\text{CH₃C(O).O.CH₂.CH₂} & \rightarrow \text{CH₃C(O).O.CH₃} \\
\text{O.COH₃} & \rightarrow \text{O.COH₃} \\
\text{O.COH₃} & \rightarrow \text{O.COH₃}
\end{align*}
\]
The resins as a class are colorless, odorless, non-toxic and have good aging characteristics. The initial mp (or glass transition temp) is 28°C (Ref 4). The polymer of 24,500 mw is sol in chloroform, benzene, pyridine and acetone; insol in carbon disulfide, carbon tetrachloride, cyclohexane, hexane, etc.

Polyvinylacetate has found use as a binder in expls (Ref 2, 3 and 6).

Polyvinylacetate aq emulsion for use as a binder in non-metallic cartridge cases is covered by US Mil Spec., “Polyvinyl Acetate Aqueous Emulsion (PAAE) (For use in Ammunition)”, MIL-P-50855(MU) (31 March 1971). The requirements and criteria are in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids, % range a</td>
<td>50–53</td>
</tr>
<tr>
<td>Viscosity, cps range b</td>
<td>4500–7500</td>
</tr>
<tr>
<td>Baked Insolubles, % min c</td>
<td>94</td>
</tr>
<tr>
<td>Chemic Nitrate Catalyst, % range d</td>
<td>43–46</td>
</tr>
<tr>
<td>Color</td>
<td>dark green</td>
</tr>
<tr>
<td>Specific Gravity, deg range e</td>
<td>48.5–49.5</td>
</tr>
<tr>
<td>Workmanship f</td>
<td>Free of impurities such as wood chips, oil and solvents not specified</td>
</tr>
</tbody>
</table>

a – Gravimetrically
b – By use of a Brookfield Viscosimeter
c – Gravimetrically
d – By any acceptable procedure
e – By using a std Baumé hydrometer calibrated for the specified range
f – By inspection


Polynvinyl Alcohol. (PVA, Albyl, Resistoflex, Solvar). A polyhydric alcohol polymer used chiefly as the starting material for Polyvinyl Nitrate (PVN) (qv), (C_2H_4O)_x or

![Chemical structure](image)

mw (44.065)_x; white to cream colored powd; softening pt at 200°C with decompt; d 1.329g/cc. Sol in hot and cold w; insol in petr solvents. Prepn is from polyvinyl acetates by replacement of the acetate groups with hydroxyl groups. Using an alkali or mineral acid catalyst the alcoholysis will proceed quickly in a methanol-methyl acetate mix. The alcohol has a flash pt of 175°F (open cup).

PVA is also used as a polymer binder for rocket propants (Ref 4).

### Polyvinyl Chloride

(Chloroethene homopolymer, Chloroethylene polymer, PVC, Vybak, Geon, Breon, Welvic, Deckor, Vinacort, Ultron, Vinylite, Koroseal, Marval). A synthetic thermoplastic polymer; white powder or colorl granules;

![Chemical structure](image)

avg mw about 60000 to 150000; tasteless, odorless, nontoxic; combustible but self-extinguishing; d 1.406g/cc. Solvents for unmodified PVC of high mw: cyclohexanone, methyl cyclohexanone, dimethyl formamide, nitrobenzene, tetrahydrofuran, isophorone, mesityl oxide. Solvents for lower polymers: dipropyl ketone, methylacyketone, methyl isobutyl ketone, acetonyl acetone, methylethyl ketone, methylene chloride. Prepn by polymerization of
vinyl chloride by suspension, emulsion and solvent methods. May be copolymerized with up to 15% of other vinyls (Refs 6, 8 & 12).

PVC is used in pyrotechnics as a chlorine donor for improved color saturation in flare, signal and tracer formulations (Refs 1, 2, 3, 4, 5, 9 & 11).

PVC is also employed in Polyvinyl Chloride Plastisol Propellants. In many ways plastisol propellants are similar to the many composite propellants which have binders comprised of polyesters, acrylates, epoxies, polysulfides, polyurethanes, or polybutadiene-acrylic acid. They all contain 75-80% by wt of finely divided inorganic solids uniformly dispersed in a continuous matrix of organic elastomeric binder. They all utilize the same inorganic oxidizer (normally Amm perchlorate) and the same powdered metals (usually AI) to enhance performance, and they all are made by thoroughly mixing the solid ingredients in a nonvolatile liq to form a viscous slurry, deaerating the mixed slurry to remove entrapped air or other gases, casting the deaerated slurry into molds of the desired shape, and solidifying the mass.

It is in the technique of solidifying the mass that plastisol propellants differ markedly from composite propellants. In composite propellants, the nonvolatile liq is comprised of monomers or low mw prepolymers. Solidification is accomplished by completion of the polymerization reactions. Much attention must be given to the degree of completion of these reactions during manuf so as to minimize changes in physical properties as a consequence of continued slow polymerization, so-called “post-cure”, following manuf.

In plastisol propellants, however, all polymerization reactions are complete before propellant manuf begins. Solidification is accomplished thru solvation (or soln) of the solid resin (or polymer) particles in the nonvolatile liq, which has been selected to be a plasticizer for the resin. Solvation or “curing” is accomplished by heating to a temp at which the resin particles dissolve rapidly (within a matter of a few minutes) in the plasticizer to form a gel which on returning to room temp has the characteristics of a rubbery solid (Ref 7).

Ref 7 reviews the characteristics and manuf of PVC plastisol propellants. Information is given on compn, uncured propellant flow, curing time, variation of physical properties with temp of cure and use, combustion products, safety characteristics, and manuf techniques. Effects of oxidizer content (Amm or K perchlorate) on specific impulse, flame temp, d, and burning rate are shown. Burning rate is correlated with oxidizer particle size. Wide variation of burning rate by use of additives and fine metal wires is demonstrated, and the effects of Al and Mg on specific impulse and burning rate are covered.

PVC plastisol propellants are employed in sounding rockets, jets, aircraft, control motors, tactical weapons and ship models. However, they are not case-bondable (Ref 10).

The requirements of the US Armed Forces for PVC are covered by two Military Specifications: “Polyvinyl Chloride (For Use in Pyrotechnics)”, MIL-P-10307A (15 May 1965); and “Polyvinyl Chloride, Plasticized”, MIL-P-47136 (24 May 1974).

The requirements of MIL-P-20307A are as follows: color, white; loss in wt at 135°C, 0.5 percent (max); ash, 0.1 percent (max); chlorine, 55.7 to 57.7 percent; specific viscosity, 0.50 to 0.70 centipoises; bulk density, 0.40 to 0.60g/ml; granulation, 95 percent min thru US Standard Sieve No 100, and 30 percent max thru US Standard Sieve No 325.

MIL-P-47136 covers one formulation of plasticized PVC used in the production of flexible tubing, cord, film, sheet, and other various extruded shapes. The Specification requirements are concerned with electrical, mechanical and physical properties and shelf life.

Polyvinyl Nitrate (PVN). \( (\text{C}_2\text{H}_3\text{NO}_3)_n \); mw 89.05\% N; theor N 15.75\%; OB to CO\(_2\) -45\%; OB to CO -9\%; with a low degree of polymerization the product is a white powder, while nitrates of a high degree of nitration are in the form of tough white strands; the color is white to buff depending on method of prep; softening pt 30-50\(^\circ\); deflagration pt ca 175\(^\circ\); Q\(_V\) 275.6kJ/kg; Q\(_G\) 1180kJ/kg; it is readily inflammable and burns without melting (Ref 16).

PVN was first prep'd in Ger in 1929 (Ref 1) by the nitration of polyvinyl alc with mixed nitric-sulfuric acid. The highest yield was 80\% but the product contained only 10\% N, against a theoretical value of 15.75\%. It detonated when heated.

Burrows and Filbert (Ref 2) improved the process of nitration by using straight nitric acid and keeping the oxidation to a minimum by conducting the operation in an atm of inert gas such as N\(_2\) or CO\(_2\). They claimed that products with as high as 15\% N could thus be obtained.

Noma, Oya and Nakamura (Ref 5) examined the reaction of nitrating polyvinyl alc and concluded that neither nitration with a mix of nitric and sulfuric acid, nor nitration with nitric and acetic acid can bring about the esterification of all of the hydroxyl group, probably due to simultaneous hydrolysis. They recommend nitrating either with a comp of nitric acid and acetic anhydride or a soln of nitric acid in carbon tetrachloride, whereby a higher nitrated product, softening at a temp of 40-50\(^\circ\) is obtained.

Deans and Nicholls (Ref 8) prep'd polyvinyl nitrates with nitrogen contents ranging between 13-15\%. They found its structure to be unstable, apparently decompg at RT. The Abel heat test at 70\(^\circ\) was more sensitive than for NC. The Trauzl Pb block test indicated high explosive power (153-341cc vs 255cc for TNT). The impact test using a Rotter Impact app gave values of 30 to 335cm vs 158cm for TNT. On standing, the impact values decreased, indicating increased sensitivity. The ignition pt range of 160-78\(^\circ\) was below that of NC (ca 200\(^\circ\)).

Chédin and Tribot (Ref 6) conducted extensive investigations on methods of prep of PVN, after WWII, in the Laboratoire Central des Services Chimiques de L'Etat Paris. They claimed that products with N content as high as 15.7\% were obtained.

LeRoux and Sartorius (Ref 10) studied PVN prep'd from both low and high viscosity polyvinyl alca. With low viscosity PVN, a max N content of 14.48\% was obtained compared with 13.43\% for high viscosity PVN. They reported Trauzl Pb block values ranging from 102cc for high viscosity to 113.5cc for low viscosity material. They also found that the detonation of PVN is propagated with a rate similar to that of NC of the same N content. The rate of detonation of PVN contg 13.4\% N, in 30mm diameter cardboard cartridges was:

<table>
<thead>
<tr>
<th>Density, g/cc</th>
<th>Detonation Rate, m/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>2030</td>
</tr>
<tr>
<td>0.6</td>
<td>3450-3520</td>
</tr>
<tr>
<td>1.0</td>
<td>4920-5020</td>
</tr>
<tr>
<td>1.4</td>
<td>6090</td>
</tr>
<tr>
<td>1.5</td>
<td>6560</td>
</tr>
</tbody>
</table>

Preparation (Typical procedure). Five g of pulverized polyvinyl alc (contg 10% moisture), previously screennd thru a No 30 sieve (metric), were gradually introduced during about 1 hr into 100ml of 99-100% nitric acid. The acid was stirred and maintained at -8\(^\circ\) by cooling thruout the addition, and for an additional 2 hrs (a total of 3 hrs). The resulting slurry was slowly drowned in an equal volume of ice w, vigorously stirred. After filtering off the white powder, it was washed with w to neutrality, and then allowed to stand for 12 hrs in pure w. The same operation (washing and standing for 12 hrs) was repeated using 95% alc, and then 12% Na bicarbonate soln. Finally, the powder was washed with distilled w until neutral, dried in air and then in vacuum; yield 96\%.

Note: The N detn was made by the Dumas method as modified by P. Jovinet and S. Courteau [MemServChimEtat 32, 16 (1945) and Etat Francais, FrP 510911 (1946)], because other methods, such as the nitrometer or the Kjeldahl, did not give reliable results.

This product was sol in acet, NG and DEGDN;
insol in 95% alc. Its thermal stability, as judged by the 72° Abel heat test and the Bergmann-Junk test, was satisfactory.

It was recommended for use in double base propulants, e.g., in the combinations NC+NG+PVN or NC+EGDN+PVN

PicArsn PVN, Preparation and Properties. Polyvinyl alc was mixed with acetic anhydride and the mixt cooled to -5°; a large excess of nitric acid was added gradually with cooling and stirring, maintaining the temp below 20°. When the nitration was completed, the mixt was poured slowly into a large amt of cold w. The resulting white ppt was filtered off, and purified by boiling in frequent changes of w.

The dried product had the following properties:

- **Nitrogen content**: 14.86%
- **Explosion temperature**: 265° (5 sec)
- **Friction pendulum test**: Steel shoe, crackles; fiber shoe, unaffected
- **Hydrolysis test**: 240 hrs; 5.07% caled as nitric acid
- **Hygroscopicity**: At 30°, 90% RH, 0.62% wt gain
- **Heat of combustion**: 2960cal/g at C
- **Heat of explosion**: 900cal/g; gas vol 838cc/g
- **100° Heat test**: % loss 1st 48 hrs, 1.9; 2nd 48 hrs, 2.1; no expln in 100 hrs
- **134.5° Heat test**: Salmon pink color in 20 mins; red fumes in 25 mins; expln in 300+ mins
- **Impact sensitivity**: Using PicArsn app with 2kg wt., 4° vs 5° for dextrinated Pb Azide and 3° for pure Pb Azide
- **65.5° Kt test**: 60+ mins
- **Sand test**: Using a 200g bomb, 49.9g vs 48.0g for TNT
- **100° Vacuum stability test**: 11+cc in 16 hrs
- **120° Vacuum stability test**: 11+cc in 16 hrs

(Ref 13)

Daume and Breitenmoser, in a 1972 patent (Ref 14), describe a process to prepare stabilized PVN from the crude product. They found that pure and stabilized PVN, usually with a N content greater than 15% can be produced from raw, decomposable PVN, resulting in a free-flowing, noncaking powder. Their process consists of (a) providing a soln of raw acid contg PVN in an org solvent; (b) neutralizing or rendering the soln slightly alkaline; (c) separating the soln from nondissolved products of the neutralization; introducing the purified soln of step (c) into a hot pptg bath in which the organic solvent is insol or only partially sol, whereby the solvent is stripped and stabilized PVN is pptd. The rate of introduction of the purified soln corresponds to the stripping rate of the solvent so that steady-state conditions are maintained. A solvent is selected in step (a), the bp of which, or the azeotropic bp of which, with the pptg bath is below the bp of the pptg bath. As the pptg bath, either pure w or an aq medium which contains certain additives is preferably used. With aq pptg baths, such solvents are preferably used in the PVN soln which form with the w an azeotrope with min bp, this usually being the case when using solvents which are not or only partially miscible with w. Examples of such solvents are esters and ketones, such as ethyl and butyl acetate or methyl ethyl ketone and methyl isobutyl ketone.

The solubility of PVN depends on its viscosity (degree of polymerization). The products of low viscosity are entirely sol in all proportions in acet, nitrobenzene and liq nitrate esters. Those of high viscosity are only partially sol, causing strong coloring of the soln.

The ease of N determination in PVN samples appears to be a function of the degree of polymerization. The nitrometer method gives consistent results, but are about 0.6% lower than the true values (Ref 6). Difficulty is experienced with high viscosity PVN. These products dissolve slowly in sulfuric acid, and give scattered results. Analytical methods based on titanic chloride, Devarda’s alloy, or the Dumas method appear to be applicable for all products (Ref 6 & 11).

PVN is a highly energetic substance which computer simulation calcns indicate would have higher impetus, similar flame temps, and a lower avg mw of combustion product gases compared to conventional NC in several proplnt comps. Table 1 gives such data for WC846 and M9 proplnts.

### Table 1

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>WC846 Proplnt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (13.15%N)</td>
<td>82.0</td>
</tr>
<tr>
<td>Polyvinyl nitrate</td>
<td>82.0</td>
</tr>
</tbody>
</table>

(continued)
**Nitroglycerin** 10.2 10.2  
**Dinitrotoluene** 0.7 0.7  
**Dibutylphthalate** 6.1 6.1  
**Diphenylamine** 1.0 1.0  
**Total volatiles** 0.8 0.8  
**Flame temp, °K** 2805 2811  
**Force, ft-lbs/lb** 329200 372200  
**Gas vol, moles/g** 0.04219 0.04753  
**Avg mw gas products** 23.70 21.02  
**Heat of expln, cal/g** 859 875  

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (13.25% N)</td>
<td>57.75</td>
</tr>
</tbody>
</table>
| Polyvinyl nitrate            | —   | 57.75  
| Nitroglycerin                | 40.00 | 40.00  
| Potassium nitrate            | 1.50 | 1.50  
| Ethyl centralite             | 0.75 | 0.75  
| Ethyl alc (residual)         | 0.50 | 0.50  
| Flame temp, °K               | 3799 | 3772  
| Force, ft-lbs/lb              | 382000 | 415000  
| Gas vol, moles/g             | 0.03618 | 0.03955  
| Avg mw gas products          | 27.64 | 25.28  
| Heat of expln, cal/g         | 1295 | 1303  

An investigation was conducted to determine the effect of addition of PVN to solventless colloidal proplnts (Refs 7 & 9). In general, the tensile strength is decreased, but the elongation at break is increased. There is an increase in flexibility. PVN has only a slight effect on the burning rate constant, but it increases the pressure exponent. In general, the addition of PVN complicates manuf without offering any worthwhile advantage over the standard colloidal NC proplnt.

Two factors have militated against its application – first, the tendency of atactic PVN to flow when mixed with other materials, and second, the inherently sticky nature of atactic PVN proplnt blends, leading to problems in the extrusion or molding of proplnt grains.

PVN was studied extensively by the Fr (Refs 6, 10 & 11), who found that, while PVN had expl properties comparable to NC and Nitrostarch, it could not be recommended for use in the expls industry.

The above comments were directed against atactic PVN, in which the nitrate groups are randomly orientated about the backbone of the polymer. Compositions contg atactic polymer are tacky or semi-solid at RT. The introduction of stereoregularity into the PVN chain results in a more crystalline material. The feasibility of prep stereoregular PVN has been demonstrated (Ref 15), and studies are currently being directed toward its evaluation.


**Ponzio Reaction.** The formation of phenyl-1,3-dinitromethane from benzaldehyde by oxidation with nitrogen dioxide in eth (Refs 1 & 2)

\[
\text{CH} = \text{NOH} \xrightarrow{\text{N}_2\text{O}_4} \text{CH(NO}_2\text{)}_2
\]

The nitration of phenyl1,3-dinitromethane yields m-nitrophényldinitromethane, m-O_2N_C6H_4_2, which was reported by Milone and Mass [Gazz 70, 196 (1940)] to be a more powerful expl than TNT or 3,5-dinitrophenyl-1,3-dinitromethane, (O_2N)_2C_6H_3.CH_2(NO_2)_2

*Refs:* 1) G. Ponzio, Gazz 27 [1], 171 (1897); JPraktChem 73 [2], 494 (1906); Gazz 36
Popped Corn. Ground popped corn is used for producing Dynamite of low d; other ingredients include NG, AN, Na nitrate, etc
Ref: N.G. Johnson & S.G. Baker, Jr, USP 1687023 (1928) & CA 22, 4821 (1928)

"Popping": A term used to designate the heat treatment of empty or fired small arms ammo cartridge cases prior to shipping them as scrap. This treatment is necessary to insure that no unfired primers remain among the cartridges.

Poseidon. A submarine-launched missile with about twice the payload of a Polaris A3 (qv). The Poseidon C3 is built by Lockheed and can be fired from existing Polaris launch tubes with very little modification of the tubes. It has a length of 34 ft, a diameter of 6 ft, a launching wt of about 60,000 lbs, and a range of 2875 miles. The Poseidon has already been tested with a MIRV payload, reported to consist of more than ten separate warheads, each with a yield of some tens of kilotons

Potassium. K; aw 39.102; at no 19; valence 1; soft; silvery metal, rapidly oxidized in moist air; body-centered cubic structure; mp 63°C; bp 770°C; d 0.862g/cc. Sol in liq ammonia, aniline, Hg and Na
K is highly toxic by inhalation and ingestion and is a strong irritant. It is a dangerous fire risk; reacts with moisture to form K hydroxide and hydrogen. The reaction evolves much heat causing the K to melt and splatter, also igniting the oxygen. K metal will form the peroxide and superoxide at room temp even when stored under mineral oil; it may expid violently when handled or cut. More than 150 reported hazardous reactions involving K with other chem species are documented in Ref 6
Metallic K in admixtures with Ag or Hg oxides or chlorides, or in contact with chlf or carbon tetrachloride, can be expld by strong impact (Ref 3). Such mixts were proposed by Staudinger (Ref 1) for use as initiating expls for blasting or in bursting projectiles.

Davis and McLean (Ref 2) studied the expl reaction between metallic K or Na and chlf more closely. They stated that if a test tube contg some chlf, and an ampule with K or Na, were dropped onto a concrete surface from a height of about 6 ft, a loud report is produced accompanied by a bright flash

Potassium Azide. See Vol 1, A594-R to A596-R

Potassium Dinitrobenzofuroxan (KDNBF). See Vol 2, B68-R

Potassium Dinitroethane. See under 1,1-Dinitroethane in Vol 6, E164-L

"Potassium" Dynamites (Dynamite à la Potasse). A series of expls proposed in 1873 by the British Dynamite Co, Ltd (which later became the Nobel Explosives Co, Ltd), which consisted of NG 15, saltpeter 70–75, plus paraffin and powdered charcoal 7–17%. Another mixt contained NG 18, saltpeter 71, charcoal 10, and paraffin 1%

In Fr, three varieties were manufctd: Arles; NG 25, K nitrate 63 and charcoal 12%; Cugny or Dynamite No 2; NG 48, K nitrate 39, and cellulose 12%; Arles et Cugny or Dynamite No 3; NG 22, K nitrate 66, and charcoal 12%
Ref: Daniel (1902), 636

Potassium Ethylenedinitramine. See in Vol 6, E244-L
Potassium Fulminate. See in Vol 6, F223-L

Potassium Nitrate. See in this Vol, N34-R

Potassium Nitride. See under Potassium Azide in Vol 1, A594-R to A596-R

Potassium Nitrite. See in this Vol, N108-L

Potassium Nitroethane. See in Vol 6, E146-L

Potassium Picrate. See under Picrates in this Vol

Potatomeal or Potatopulp Explosives. Expls made by drying raw potato pulp, mixing it with about 80% of its wt of K chlorate, granulating and drying the mixt, and tumbling with graphite to coat the granules

Refs: 1) D.M. Stirton, USP 995579 (1911) & CA 5, 2725 (1911) 2) G.M. Peters, USP 1048578 (1912) & CA 7, 703 (1913)

Pot de Feu (Fire Pot). See under Cannon in Vol 2, C26-L

Potentite. A smokeless powder, prep'd in the 1880's by the Cotton Powder Co, Ltd of Engl by mixing wet NC (59.5% on a dry basis) with 40.5% K nitrate. It was also called "Cotton Powder of Liverpool" (Ref 1). Pepin Lehalleur (Ref 2) refers to Potentite as being an NC expl used prior to WWI in demolition blocks, contg Guncotton 50, K nitrate 50%

Refs: 1) Daniel (1902), 636 2) Pepin Lehalleur (1935), 354

Powder-Air Explosions and Detonations.
Two-phase detonations involving fuel drops or solid particles and a gaseous oxidizer have been observed (Refs 8, 9 & 11). Detonations in fuel drop and gaseous (air or pure oxygen) mixts have been studied in greater detail because of their relevance to FAE (see Vol 6, F3-L to F4-R) and liq rocket engine instabilities (Refs 8, 11, 12, 13 & 16). It has been shown that the fuel drop size and number density can affect the ignition and detonation characteristics.

Currently, liq fuels are used in all fuel-air munitions (Refs 8 & 12). The fuel drops are created by the techniques of expl dissemination. Due to the large effect of the drop size and drop distribution on the detonation characteristics, many restrictions are placed on both the method of dissemination and the final design of the munition. In the case of solid fuels, the particle size can be accurately controlled, allowing other dissemination techniques to be utilized. This flexibility in design criteria can lead to improvement in overall munition performance. Solid fuels also have other practical advantages over liqs. Higher charge densities can be achieved in loading with solids than with liqs, and thermal expansion problems during storage can be minimized.

Solid particle-gaseous oxidizer systems have been studied because of applications to propinns and expls (Refs 5 & 14), and hazards due to dust explns (Refs 1, 3, 4, 6, 7, 10 & 15). Strauss (Ref 9) reported on a heterogeneous detonation in a solid particle and gaseous oxidizer mixt; the study concerned Al powder and pure oxygen in a tube. Detonations initiated by a weak source were obtained in mixts contg 45–60% fuel by mass. Measured characteristics of the detonations agreed with theoretical calns within about 10%, and detonation pressures of up to 31 atm were observed. With regard to solid particle-air mixts, detonations have not been reported; only conditions for expln have been studied (Ref 2).

Lu, Vyn, Sandus and Slagg (Ref 17) conducted ignition delay time and initiation studies on solid fuel powder-air mixts in an attempt to determine the feasibility of solid-air detonations. The materials investigated included Al, Mg, Mg-Al alloy, C and PETN. Ignition delay time was used as a method of screening the candidate fuels for further work in initiation studies which determined detonation wave speed, detonation pressure, detonation limits, initiation requirements, and the effect of particle size and confinement. The testing showed the importance of large surface area per unit mass, since the most...
promising materials were those with small particle sizes and nonspherical shapes such as Al flakes. Shock tube initiation studies were performed on Al flake-air suspensions using an \( \text{H}_2-\text{O}_2 \) driver and in a chamber with central point ignition. The results gave strong though inconclusive indications of the occurrence of detonations.


Powder Bags. See Cartridge Bags in Vol 2, C77-L

Powder, Black. See Black Powder or Gunpowder in Vol 2, B165-R ff

Powder Chamber Pressure Measurements. See Chamber Pressure in Vol 2, C147-R

Powder Explosions. See under Coal Dust; Explosion Hazards from its Uses in Vol 3, C359-R; Dust Explosions in Vol 5, D1578-R; and Powder-Air Explosions and Detonations in this Vol

Powder Metallurgy. The content of this article is a verbatim reproduction of the ref “Conventional powder-metallurgy (PM) processing is a fabrication method characterized by high productivity and low-cost yields. Parts are produced to ‘net/near-net’ shapes having good dimensional accuracy and surface finish.

The method of producing components from metal powder is to prepare a PM compact by pouring blended metal powders into a die cavity and applying pressure. The cold-pressed (green) compact is then heated for an appropriate time at a temperature such that the metal particles ‘sinter’ or fuse together, being densified to approximately 85 per cent theoretical.

Consequently, the mechanical properties normally are characterized by lower strength, lower ductility, lower impact strength, and reduced fatigue endurance.

The use of PM products in Army materiel fulfills a variety of special applications. These products would include magnetic materials, refractory metals, controlled-porosity materials,
nonalloyable metals, friction materials, metallic-nonmetallic mixtures, hard materials, etc. However, military weapon systems contain many small structural components generally made of low-alloy or plain carbon steel and the use of PM products for these components is quite limited.

PM steel-processing techniques have not been used for the fabrication of structural parts or critical components because, as stated previously, the properties of sintered steel parts have not approached the mechanical properties or reliability of wrought materials. The reason for this is attributed to residual porosity and chemical inhomogeneity inherent in pressed and sintered 'blended' metal powders.

Advances in powder metallurgy have brought the technology to a point where it could be applied advantageously to the production of highly stressed, critical components. Specifically, PM forging now can replace the conventional forging of certain low-alloy steel components. A PM preform could be made using recently developed prealloyed steel powders, and full densification could be achieved by hot precision forging to final configurations after the sintering operation.

This procedure, a logical consolidation of PM and forging methods, would resolve the inhomogeneity and porosity problems associated with PM products and combines the cost advantages of powder metallurgy with the structural integrity of forged components.

Program Initiated. An Army Manufacturing Methods and Technology (MMT) program was initiated in 1969 and had two objectives. The first was to document a process for the forging of prealloyed steel powders capable of producing complex-shaped, high-performance components having quality levels equivalent to conventional forgings but at a significantly lower manufacturing cost.

It is common knowledge that the use of PM processing techniques is greatly expanded as production quantities are enlarged. This is attributed to the higher tooling costs required for 'net/near-net' forgings. Since Department of Defense arsenals usually are concerned with smaller production orders compared with the private sector, full realization of potential cost savings would not be achieved.

Therefore, the second objective, equally important, was to share the results of this program not only with other DOD organizations but also with the private industrial sector. Since industry is concerned with larger production orders, the DOD procurement posture would be improved substantially through the shared knowledge and established standardization specifications. This, in fact, is the goal of all MMT programs.

A 2-phase program was conducted. The first phase was a materials and process study. The second phase dealt with the manufacture of a selected high-performance weapon component in prototype quantity to demonstrate the applicability of the developed PM forging process. A processing specification and an economic evaluation of the developed manufacturing process also was included.

The compressibility and sinterability of a large variety of 4,600 prealloyed steel powders, mixed with sufficient graphite to give 0.40 per cent carbon, were investigated. Sintered compacts were forged at selected temperatures over the range of 1,400 to 2,200 degrees Fahrenheit using both conventional and minimum-deformation (flash-free) tooling. Apart from forging temperature, the variables investigated were preform porosity, protective coating, and forging pressure or amount of reduction.

The forgings were evaluated by density, microstructure, surface finish, tensile strength, notched impact strength, ductility, and fatigue strength measurements.

For further process optimization, the minimum-deformation forging was selected primarily because it was capable of producing a high-quality flash-free forging with no draft angles, thus eliminating subsequent machining steps.

Results of the forging study on the selected 4640 composition have shown that PM forgings were competitive with wrought materials from a property standpoint. Tensile and yield strength were density dependent and comparable to wrought materials in the range of 98 per cent or higher density. Ductility and impact properties were very sensitive to minor amounts of residual porosity.

However, PM forgings with near-theoretical density (99 per cent plus) when combined with microstructure uniformity and low interstitial
content provided notched impact strength and ductility comparable to bar-stock forgings.

The viability of the developed minimum deformation PM forging process was demonstrated in the production of the accelerator for the M85 caliber .50 machine gun. Through the use of PM forging methods, the production sequence for the accelerator was reduced from 6 to 2 forging operations and from 23 to 7 machining operations. This resulted in reducing the cost of the accelerator from $95.00 (using conventional forging sequences) to an estimated cost of $30.00 for the PM accelerator.

It was concluded that any candidate component can be produced using PM forging techniques at a cost at least 50 per cent lower compared with conventional forging processes. The accelerators were endurance-tested and exceeded all requirements in the standard room-temperature tests. The accelerators also withstood the test firing of more than 10,000 rounds at minus 65 degrees Fahrenheit with no failures being experienced.

A Military Specification (MIL-F-45961), the first of its kind, for prealloyed steel powder forgings was then drafted and has been accepted as a standard by Department of Defense and commercial organizations. The significance of this work is that the improved PM manufacturing technology is applicable to all weapon systems which require complex-shaped steel forgings.

Future Prospects. Evaluations were made of the M85 weapon, and it has been determined that 26 components could be made at greater than 50 per cent cost reductions if PM forged products, rather than conventionally forged parts, were used. Engineering Change Proposals (ECP's) have been processed, and PM forgings are now specified as alternate products for the 26 components. Evaluation of the M60 machine gun has shown that 22 components can be produced more cheaply when PM products are used.

The significance of this work is that this new technology is applicable to all weapon systems which require complex-shaped components made of steel forgings. Evaluation of all future weapon systems will continue to determine which components can be produced more economically using PM forged products.

To assist the transition to a more versatile production capability, an MMT program entitled 'Computerized PM Forging Design' is proposed for fiscal 1977. This program will provide the required die design technology to expand this new manufacturing method. In other words, there are many components which could be more economically produced by PM forging if a production order called for, say, 15,000 pieces.

Through the use of computer-aided graphics, the trial-and-error method of forging-die development would be eliminated and tool setup costs would be minimized. Consequently, the minimum 'go/no-go' production order for PM forged products could be reduced to 7,500 pieces or even less.


Power Cartridge. Initiators in which a proplnt compn is used for initiation and for generating heat and pressurized gas for a short duration. Power cartridges contain an ignition primer and a main charge of a pressure producing proplnt, mounted in one casing. The ignition primer initiates the main proplnt charge which consequently generates gas in the required quantity and temp. The gas thus produced can be used for numerous work functions, for example, for pushing a piston, inflating a flotation device, or fracturing a diaphragm.

The amt of gas generated is relatively small, the major energy results from the gas temp. A typical power cartridge produces a pressure of 4400psi in a closed test chamber of 10cc volume in 5 to 10 millisecc after initiation of the cartridge. Pressure ranges in these cartridges are generally from 100psi to 10000 psi, although those with a pressure capacity of 70000psi have been developed for special applications.

Power cartridges are ideally used for the actuation of separation nuts and bolts, valves, ejection systems, pressure-actuated pumps, switches and piston devices, such as pyrotechnic
cutters for cables, straps, reefing lines, hoses and tubes. In spacecraft and missile systems they have been utilized for umbilical release, airborne emergency separation systems, thrusters, pin pullers, drogue chute mortars, line cutters, thrust reversal systems, termination devices, and separation systems for fairings and nose cones


Power of Explosives. In its normally used context, power of an expl is a misnomer. It is generally accepted that power of an expl is a measure of its strength, its blasting action or available energy, and not necessarily a measure of its rate of energy delivery, which is indeed the true definition of power. Further confusion arises because another frequently used expl term, called brisance, is sometimes erroneously equated with power. Brisance is a measure of the ability of an expl to shatter material in its immediate vicinity. The fundamental property of an explosive that determines brisance is its detonation pressure (see Vol 2, B265-L). The power of an expl (we bow to accepted usage and will keep referring to power rather than the correct terms such as strength or blasting ability), on the other hand, is a measure of the ability of an expl to do work such as blasting down rock or propelling a chunk of metal. The fundamental expl property that determines its power (or better, available work) is its heat of detonation. Q (see Vol 7, H38-L), or the related quantity, n_{T_j}, where n_j is the number of moles of gas under steady (Chapman-Jouguet) detonation conditions and T_j is the detonation temp \(^b\).

As will be shown below, a more exact dependence is that power is proportional to Q-q (rather than just Q), but q, the residual heat of the detonation products, is usually quite small compared to Q.

According to Cook (Ref 2), the energy available to do external work (we continue to.miscall it power) is

\[
A = - \frac{V_f}{V_i} \int_{T_i}^{T_f} PdV = \int_{T_o}^{T_f} C_v dT - \int_{T_o}^{T_f} C_v dT = Q-q
\]

where P = pressure, V = volume, T = temp, C_v = specific heat of the detonation products, and the subscripts o, i & f refer to ambient, initial and final states respectively. The initial state is usually taken to be that achieved in a constant volume expn for which P_v = P_i/2; T_v = (T_i + 1)(T_i)/2P = 4/6 T_j; and n_v \geq n_j. \(^b\) The final state is the state of product expansion, after which no more useful work is available

As pointed out by Cook (Ref 2), there is no unequivocal method of computing A for expls that produce appreciable arts of condensed phase (solid) products. Cook suggests the use of an empirical relation

\[
A = Q' + \frac{1}{2} Q''
\]

where Q' is the heat of detonation computed solely for gaseous detonation products; Q'' is the heat of detonation computed solely for condensed phase products

Andreev & Belyaev (Ref 4) show that

\[
A = Q \left[ 1 - \left( \frac{P_f}{P_i} \right)^{T_f/\Gamma} \right]
\]

For military expls (P_f/P_i)_{max} = 10^{-3}, which for \(\Gamma=3\) gives A = 0.99 Q. For commercial expls such as AN/FO, P_f/P_i = 5 x 10^{-3} and \(\Gamma = 2.1\) (Ref 8), therefore A = 0.94 Q. Thus A = Q appears to be a rather good approximation

Explosion Power is always measured in relative terms, \(Q\), relative to a standard expl and expressed as a percentage. For military explosives the consensus standard is TNT, and for commercial expls the standard is usually Blasting Gelatin (see Vol 2, B211-R). Three measurement methods are in common use: 1) Ballistic Mortar; 2) Trauzl block; 3) Underwater explns; and 4) one method — cylinder expansion — that is now used at Lawrence Livermore Laboratories

The ballistic mortar method is described briefly in Vol 1, p VII. Basically this test consists of firing a standard weight of expl (usually 10g) in a suspended mortar closed with a tightly fitting steel projectile. The angle of recoil of the mortar is measured and compared to the recoil produced by the same weight of a standard

\(^a\) Not quite correct; see discussion below

\(^b\) In reality, since most explosives are oxygen deficient, n_v \geq n_j because P_v < P_i and less solid carbon will be formed (see article on Products of Detonation in this Vol). Consequently n_vT_v \geq n_jT_j since n_v > n_j but T_v < T_j.
expl. Although the measurements are capable of high precision, the power or strength thus obtained is difficult to relate to the ability of the test expl to break rock, propel metal, etc. The loading d in the ballistic mortar is much lower than that used in practice. Consequently, neither the initial nor the final states obtained in the mortar correspond to what is obtained in actual practice. Gas leakage from the mortar results in additional uncertainty. It is also unfortunate that TNT is commonly used as the standard mortar charge. TNT detonation products compress very strongly on pressure and thus on loading d. However, for nearly oxygen-balanced Dynamites which generate mostly gaseous detonation products, the ballistic mortar should provide fairly reliable data on the performance of these Dynamites in actual blasting.

Commercial expls have a percentage power or strength rating marked on the expl cartridge. For straight NG Dynamites this strength rating is exactly equivalent to the NG content of the Dynamite. With other energy developing ingredients in the Dynamite (AN for example) the strength is no longer directly proportional to the NG content. Thus a 60% weight strength Dynamite may contain only 10–15% NG with most of its strength contributed by AN and other ingredients.

Comparisons between ballistic mortar strengths and heats of detonation relative to TNT are shown in Table 1 (the mortar values were taken from Ref 5 and the heats of detonation from Vol 7, H41–42). Agreement is generally quite good.

Table 1
Comparison of Ballistic Mortar Strength with Observed Heats of Detonation

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Ballistic Mortar Relative to TNT</th>
<th>Heat of Detonation Relative to TNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX</td>
<td>1.50</td>
<td>1.48</td>
</tr>
<tr>
<td>RDX</td>
<td>1.50</td>
<td>1.51</td>
</tr>
<tr>
<td>PETN</td>
<td>1.45</td>
<td>1.49</td>
</tr>
<tr>
<td>NG</td>
<td>1.40</td>
<td>1.48</td>
</tr>
<tr>
<td>Comp B</td>
<td>1.33</td>
<td>1.20</td>
</tr>
<tr>
<td>Tetryl</td>
<td>1.30</td>
<td>1.14</td>
</tr>
<tr>
<td>50/50 Pentolite</td>
<td>1.26</td>
<td>1.23</td>
</tr>
<tr>
<td>Picric Acid</td>
<td>1.12</td>
<td>1.03</td>
</tr>
<tr>
<td>DATB</td>
<td>1.00</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Based on calorimetrically measured values given in Ref 7. We have arbitrarily used 1.00 kcal/g as the heat of detonation of TNT. For highly confined TNT \( H_d = 1.09 \text{kcal/g} \) and 1.03 kcal/g for partially confined TNT.

Some additional mortar strengths are shown in Vol 2, B266–95.

In the Trauzl-block test the expl is loaded into a Pb block at a loading d near 1.0g/cc and stemmed or sealed in with a screw cap. Theoretically these measurements should correlate well with practical conditions because initial and final states in the measurement and in practice should be similar. Unfortunately the Trauzl method is not very reproducible (in part because of rupture of portions of the block by reflected shocks). Consequently no further discussion of the Trauzl-block measurements will be made in this article. Interested readers are referred to Vol 2, B266–95 and Ref 5 for Trauzl block data for many expls.

Cole (Ref 1) described methods and presented data for measuring the underwater effects of expls. Price (Ref 3) suggested that the underwater effectiveness of an expl can be indicated by the sum of its shock wave and bubble energy equivalent wts (in her paper relative to 50/50 Pentolite). In Table 2 we compare such indices of underwater performance (but relative to TNT rather than Pentolite) with relative heats of detonation. We used 1.09 kcal/g for the heat of detonation of TNT under the assumption that deep water provides good confinement. Note that agreement is not as good as in Table 1, but

Table 2
Comparison of Underwater Effectiveness of Explosives with their Heat of Detonation

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Relative Underwater Effectiveness</th>
<th>Relative Heat of Detonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNETB</td>
<td>1.28</td>
<td>1.35</td>
</tr>
<tr>
<td>PETN</td>
<td>1.25</td>
<td>1.37</td>
</tr>
<tr>
<td>HMX</td>
<td>1.19</td>
<td>1.36</td>
</tr>
<tr>
<td>RDX</td>
<td>1.16</td>
<td>1.38</td>
</tr>
<tr>
<td>Comp B</td>
<td>1.11</td>
<td>1.10</td>
</tr>
<tr>
<td>50/50 Pentolite</td>
<td>1.09</td>
<td>1.13</td>
</tr>
<tr>
<td>Tetryl</td>
<td>1.08</td>
<td>1.05</td>
</tr>
<tr>
<td>TNT</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
there is certainly a correlation trend, i.e., expls with large heats of detonation have a greater underwater effectiveness than expls which have smaller heats of detonation. The effectiveness of aluminized expls cannot be correlated with their heat of detonation since there are no reliable values for the latter.

Incidentally, air blast effects correlate much better with computed Q's rather than calorimetrically measured Q's (Ref 6).

A fairly recent method of measuring expl energy (power in our convention) depends on accurate determination of the expansion of an explosively-driven metal cylinder (Refs 7 & 8).

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Relative Cylinder Expansion Energy (Tangential)</th>
<th>Relative Heat of Detonation (on a volume basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX</td>
<td>1.79</td>
<td>1.72</td>
</tr>
<tr>
<td>BTF d</td>
<td>1.72</td>
<td>1.61</td>
</tr>
<tr>
<td>PBX 9404</td>
<td>1.66</td>
<td>1.56</td>
</tr>
<tr>
<td>PETN</td>
<td>1.615</td>
<td>1.61</td>
</tr>
<tr>
<td>LX-04</td>
<td>1.51</td>
<td>1.50</td>
</tr>
<tr>
<td>Comp B</td>
<td>1.36</td>
<td>1.26</td>
</tr>
<tr>
<td>50/50 Pentolite</td>
<td>1.29</td>
<td>1.28</td>
</tr>
<tr>
<td>XTX-8003 e</td>
<td>0.974</td>
<td>1.11</td>
</tr>
<tr>
<td>TNT</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>NM</td>
<td>0.764</td>
<td>0.806</td>
</tr>
</tbody>
</table>

d Benzotriifuroxanhexanitrosobenzene
e Extrudable PETN composition
For TNT, $\Delta H_2$ taken to be 1.63 kcal/cc

Available expln energy is then correlated with the kinetic energy of the metal cylinder. In Table 3 we see that relative cylinder expansion energies (from Ref 7) correlate fairly well with relative heats of detonation if the latter are taken on a per unit volume basis.

Thus we see that there is reasonable correlation between power of an expl, measured in a variety of ways, and its heat of detonation. Earlier in this article it was mentioned that power can also be correlated with $n_T_j$. The latter correlation follows directly from Eq (1) if $c_v \neq f(T)$. With this restriction, the two middle integrals of Eq (1) give

$$c_v(T_j - T_0) - c_v(T_f - T_0) = c_v(T_j - T_f) = n_v R(T_j - T_f)/\gamma - 1 = \text{const} \cdot n_v T_j$$

since $R$ and $\gamma$ are constants.

Written by J. Roth


Praepositor (or Präposat). An expl similar to BlkPtr, mfnufd in the 1870’s by the International Praepositiv Co Powder Works, Millville, NJ, until the plant expld. The compn was KNitrate, S, charcoal, and “Hipposine”, the latter ingredient being finely pulverized dried horse dung. The same expl was mfnufd in Ger by the Deutsche Präpositivwke G.m.b.H., Karlsruhe in Bavaria (Ref 1).

Refs: 1) Anon, SS 9, 55 (1914) & CA 8, 1508 (1914) 2) Van Gelder & Schlatter (1927), 28

Precession. A change in the direction of the axis of a rotating body, as a spinning top, or gyroscope, the effect of which is to rotate this axis (axis of precession) perpendicular to its original direction and to the axis of the twisting forces producing the change.

When a symmetrical projectile leaves a gun barrel, it travels along the “line of fire” (also called the “line of no precession”), and at the same time spins rapidly around its long axis of gravity. The resistance forces are parallel to the line of fire, the center of pressure is at or near the apex of the projectile, there is no precession, and the projectile flies without yaw. As the force of gravity begins to draw the projectile away from the line of fire onto its curved trajectory, the direction of the resistance forces start to change, causing the center of pressure to move slowly from the apex toward the base along the ground side of the flying projectile. The change in the direction of the resistance...
forces away from the line of fire will start the precession on the long axis. From that time on, the projectile will be flying with "yaw". The greater the precession and yaw, the greater is the air resistance. They can be minimized if the projectile is symmetrically constructed (uniform wall thickness) and uniformly loaded

Refs:
1) C. Cranze, "Handbook of Ballistics" (Engl translation), Vol 1, HMSO, London (1921), 243
2) H.V. Wagner, "The Projectile in Flight", Ordn 37, No. 194 (1952), 341-44
3) OrdtTechTerm (1962), 230-L

Preisehammer Explosives. Mining explos, patented in 1864, consisting of mixts of hydrogen and oxygen
Ref: Daniel (1902), 651

Premature Explosions. See Vol 6, E380-L to E383-R


Pressing. See 1,3,5,7-Tetranitrophenothiazine under Phenothiazine in this Vol

Pressure, Detonation. Detonating condensed explos develop very high pressures. For most military explos and many of the commercial explos the pressures attained within the expl column do not depend on confinement, provided the column diameter is appreciably larger than the critical diameter of the expl. This confinement-independent pressure associated with a steady detonation is called the Chapman-Jouguet pressure or $P_{CJ}$

References to detonation pressure are scattered throughout Vol 4, eg, D230-35; D265, D463-64, and D483-93. The present article is primarily an update of the Vol 4 entries. However, its additional purpose is to bring together in a single article pertinent information on detonation pressure.

Detonation pressure may be computed theoretically or measured explt. Both approaches are beset with formidable obstacles. Theoretical computations depend strongly on the choice of the equation of state (EOS) for the detonation products. Many forms of the EOS have been proposed (see Vol 4, D269-98). So far none has proved to be unequivocally acceptable. Probably the EOS most commonly used for pressure calcs are the polytropic EOS (Vol 4, D290-91) and the BKW EOS (Vol 4, D272-74 & Ref 1). A modern variant of the Lennard-Jones-Devonshire EOS, called JCZ-3, is now gaining some popularity (Refs 11 & 14). Since there is uncertainty about the correct form of the detonation product EOS there is obviously uncertainty in the pressures computed via the various types of EOS.

The situation in expl measurements of detonation pressure is hardly more satisfactory than that encountered in theoretical computations. Although there may be reasonably good agreement among pressure measurements made by a given technique, agreement among Measurements made by different techniques for the same expl is often unsatisfactory. This state of affairs has led to what has been called "Kamlet's Complaint" (Ref 13) which in effect states that no single $P_{CJ}$ measurement is universally accepted as being correct to within 5%.

The different pressure measurement techniques alluded to in Kamlet's complaint may be grouped into particle velocity measurements, transmitted shock velocity measurements, pres-
sure transducer measurements and detonation product density profiles. Among the particle velocity measurements are the various free surface velocity ($u_{p}$) measurement techniques (Vol 4, D485-91; Ref 10, pp 5-7 to 5-10 and 5-15 to 5-18; & Ref 3), the magnetic probe techniques (Refs 7, 8 & 13), and the flash X-ray technique (Refs 2 & 3). Measurements of shocks transmitted into inert solids or water (aquarium method) have been used to obtain $P_{cj}$ (Refs 4, 6 & 8). Pressure transducer methods are described in Ref 10, pp 5-10 to 5-15, Ref 14, and Refs 5 & 17. The flash X-ray technique is also claimed to give density profiles of detonation products (Refs 2 & 3).

A good illustration of the discordance observed among several of the above methods is given in the following tabulation taken from Ref 3:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Pressure—kbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rarefraction velocity (X-ray)</td>
<td>268 ± 6</td>
</tr>
<tr>
<td>Embedded foils (X-ray)</td>
<td>275 ± 4</td>
</tr>
<tr>
<td>Protected flash gap ($u_{o}$)</td>
<td>292 ± 5</td>
</tr>
<tr>
<td>Reflection—change flash-gap ($u_{o}$)</td>
<td>312 ± 5</td>
</tr>
</tbody>
</table>

Table 1

<table>
<thead>
<tr>
<th>Technique</th>
<th>Pressure—kbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rarefraction velocity (X-ray)</td>
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</tr>
<tr>
<td>Reflection—change flash-gap ($u_{o}$)</td>
<td>312 ± 5</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Density (g/cc)</th>
<th>Det Vel (cm/μsec)</th>
<th>Transmitted Shock Vel, $u_{s}$ (cm/μsec)</th>
<th>Measured Detonation Pressure, $P_{det}$ (kbar)</th>
<th>LLL Values 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>St Line Fit 2mm</td>
<td>Model I</td>
<td>Model II</td>
<td>Model III</td>
</tr>
<tr>
<td>PBX 9404a</td>
<td>1.844</td>
<td>.881</td>
<td>.677</td>
<td>.676</td>
<td>.686</td>
</tr>
<tr>
<td>TNTp</td>
<td>1.638</td>
<td>.692</td>
<td>.561</td>
<td>.553</td>
<td>*</td>
</tr>
<tr>
<td>Pentolite2-p</td>
<td>1.644</td>
<td>.752</td>
<td>.618</td>
<td>.624</td>
<td>.630</td>
</tr>
<tr>
<td>Comp. B3,c</td>
<td>1.729</td>
<td>.798</td>
<td>.641</td>
<td>.637</td>
<td>.647</td>
</tr>
<tr>
<td>LX-04-14</td>
<td>1.858</td>
<td>.846</td>
<td>.654</td>
<td>.688</td>
<td>.660</td>
</tr>
<tr>
<td>LX-075</td>
<td>1.850</td>
<td>.859</td>
<td>.694</td>
<td>.684</td>
<td>.694</td>
</tr>
<tr>
<td>LX-096</td>
<td>1.861</td>
<td>.882</td>
<td>.662</td>
<td>.682</td>
<td>.682</td>
</tr>
<tr>
<td>LX-107</td>
<td>1.841</td>
<td>.881</td>
<td>.679</td>
<td>.675</td>
<td>*</td>
</tr>
<tr>
<td>Cyclotol8,c</td>
<td>1.757</td>
<td>.830</td>
<td>.644</td>
<td>.659</td>
<td>.668</td>
</tr>
<tr>
<td>RX-11-AY9</td>
<td>1.876</td>
<td>.625</td>
<td>.540</td>
<td>.639</td>
<td>.541</td>
</tr>
</tbody>
</table>

1 Values determined by the LLL "Standard Test for Detonation Pressure Measurement"
2 50/50 PETN/TNT average PETN particle size 10 μm
3 50/40 RDX/TNT
4 85/15 HMX/Viton
5 90/10 HMX/Viton
6 93.3/4.2/2.5 HMX/DNPA/FEFO
7 95/5 HMX/Viton
8 72/25 RDX/TNT
9 HMX/Potassium Perchlorate Formulation

Model I: $R = A_1 + A_2 + A_3 e^{A_4 \cdot t}$
Model III: $R = A_3 t + 4 A_1 A_2 \tan^{-1}(t/2A_1)$

See Ref 6

a Average of two shots
b Pressed
c Model III failed to converge to a solution
d Cast
For Comp B of slightly lower density, Jameson and Hawkins (Ref 4) measured 266 ≤ P_{CJ} ≤ 284 kbar using a shock transmission technique. The aquarium method of Rigdon and Akst (Ref 6) gave 294 ≤ P_{CJ} ≤ 304 kbar for a Comp B of slightly higher density than that of Ref 3. Clearly Kamlet's complaint is well justified, since measured P_{CJ} for Comp B vary from 266 to 312 kbar.

A good compilation of recent measurements of P_{CJ} for many military expls is given by Dobratz (Ref 11). This compilation relies heavily on measurements made at the Lawrence Livermore Laboratory (LLL). Particularly extensive measurements of P_{CJ} as a function of packing density were made at that laboratory for PETN (Ref 9).

In Table 2 the "aquarium" measurements of Rigdon & Akst (Ref 6) are compared with LLL measurements. Agreement is surprisingly good.

Some interesting results for very low density foamed PETN or expanded NC were obtained by Austing et al (Ref 5). These are shown in the tabulation below:

<table>
<thead>
<tr>
<th>System</th>
<th>Initial Explosive Density, g/cc</th>
<th>Foam Density, g/cc</th>
<th>CJ Pressure, kbars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foamed PETN</td>
<td>0.176</td>
<td>0.136</td>
<td>4.8</td>
</tr>
<tr>
<td>Expanded NC</td>
<td>.252</td>
<td>-</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>.141</td>
<td>-</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.104</td>
<td>-</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Austing's PETN measurement is in reasonable accord with the measurements of Ref 9.

In recent years the most commonly used expl in mining has been ANFO (94/6 AN/Fuel Oil). Ref 16 quotes 55 ≤ P_{CJ} ≤ 61 kbar for very large charges of ANFO.

The preceding paragraphs have been primarily devoted to a brief description of the methods of measuring detonation pressure and the presentation of selected measurement data. We have emphasized that both theory and measurements entail considerable uncertainty. Thus comparison between theory and observation is at best rather risky. Nevertheless, the P_{CJ} vs loading density...
density curves shown below (from Ref 15) are of considerable interest (Figs 1 & 2). They suggest that reasonable accord exists between the more popular types of theoretical calcs and expptl measurements. Indications are that pressure computations based on the BKW EOS are generally somewhat too high, while those based on the J23-3 EOS are a little too low. The BKWR is a modified BKW EOS which apparently has been curve-fitted to the expptl data.

Written by J. ROTH


Pressures, Gun. Pressures within a gun tube or barrel, as used in design practices. Because of the wide variations in size, wall ratios, heat dissipation, required safety actors, etc, design practices vary for the different types of weapons. Some pressure terms have significance in the design of (a) all tubes and barrels, (b) cannon tubes, (c) recoilless rifle tubes, and (d) small arms barrels, viz:

(a) For All Tubes and Barrels:

Chamber Pressure. The pressure existant within the gun barrel at any time as a result of the burning of the propint charge. This pressure normally varies from atm pressure at the time of ignition to a peak pressure which is attained when the projectile has traveled a very short distance, decreasing steadily until the projectile emerges from the muzzle. It then drops quickly to atm pressure again (Fig 1).

(b) For Cannon Tubes:

Elastic Strength Pressure (ESP). Computed true internal gas pressure in a gun at any given cross section thereof that will stress the metal at the inner layer of the wall at that section tangentially up to the max elastic limit of the metal from which the inner layer is made. Normally required to be at least 1.5 times the computed max pressure.

Maximum Pressure. Max value of the pressure exerted by the propint gases on the walls of a gun during the firing of a round.

Computed Maximum Pressure (CMP). Value of max pressure computed by means of interior ballistic formulas. It will be developed when a new gun of a particular type is fired under standard conditions with a propelling charge which will give to the projectile its rated muzzle velocity.

Rated Maximum Pressure (RMP). Value of max pressure specified in the propint specifications as the upper limit of avg pressure which may be developed by an acceptable propint in the form of propelling charges which will impart the specified muzzle velocity to the specified projectile. Normally about 2000 psi above the computed max pressure, subject to determination at the time of development.

Lower Acceptable Mean Maximum Pressure (LAMMP). Value of max pressure specified in
the propellant specifications as the lower limit for
the avg of the max pressures developed by ac-
ceptable propellent in propelling charges that will
 impart the specified muzzle velocity to the
 specified projectile. Normally about 4000psi
 under the computed max pressure, subject to
determination at the time of development

Permissible Mean Maximum Pressure (PMMP). Value which should not be exceeded by the avg of
the max pressures developed in a series of
rounds fired under any service conditions.
 Normally established as 1.08 times the rated
max pressure

Permissible Individual Maximum Pressure
(PIMP). Value which should not be exceeded
by the max pressure developed by any individual
round under any service condition. Normally
established as 1.15 times the rated max pressure

(c) For Recoilless Rifle Tubes:

Elastic Strength Pressure (ESP). The gas
pressure that will produce an equivalent stress
(based on distortion-energy criteria) at some
point in the gun that is equal to the min elastic
limit of the material at ambient temp

Elastic Strength Pressure (Hot). (ESP
[Hot]). A reduced elastic strength pressure; the
reduction is made to allow for the decreased
elastic limit of the gun materials at elevated
temps

Computed Maximum Pressure (CMP). The
gas pressure which is computed by means of in-
terior ballistic formulas to be the max gas pres-
sure developed by the gun under standard
conditions and rated muzzle velocity

Rated Maximum Pressure (RMP). The gas
pressure which should not be exceeded by the
avg of the max pressures developed by a group
of firings which will impart the specified muzzle
velocity to the specified projectile. If the RMP
is exceeded, the propellant lot is considered un-
acceptable

Lowest Acceptable Mean Maximum Pressure
(LAMMP). The gas pressure which should be
equalled or exceeded by the avg of the max
pressures developed in a series of rounds which
meet the muzzle velocity requirements

Permissible Mean Maximum Pressure (PMMP). The
gas pressure which should not be exceeded by
the avg of the max pressures developed in a
series of rounds fired under any service con-
ditions

Permissible Individual Maximum Pressure
(PIMP). The gas pressure which should not be
exceeded by the max pressure developed by any
individual round under any service condition

(d) For Small Arms Barrels:

Maximum (or Peak) Chamber Pressure.
Max value of pressure induced in the chamber
as detd by the help of a Cu crusher gage or
with a piezolectric gage. Comparison has shown
that Cu pressures should be multiplied by 1.2 to
give true peak pressures

Residual Chamber Pressure. Pressure in
chamber from time of bullet exit

Barrel Pressure. Value of pressure induced
by the propellant gases at any barrel position and
at the time that the bullet passes the particular
position. May be calc'd with the help of the
simultaneous chamber pressure

Maximum Barrel Pressure. Value of pres-
sure induced by the propellant gases at a barrel
position just passed by the bullet, and at a time
that peak pressure exists in the chamber

Proof Pressure. This pressure is about 20%
larger than that induced by the service round.
If used for barrel design purposes, it provides
some margin of safety

Refs: 1) Anon, OrdTechTerm (1962), 231–32
2) Anon, EngrgDesHndbk, “Ballistic Series,
Interior Ballistics of Guns”, AMCP 706-150
(1965)

Pressure, Influence of on Combustion of Pro-
pellants. See under Burning and Burning Char-
acteristics of Propellants for Artillery Weapons
and Small Arms in Vol 2, B346-L ff

Pressure, Influence of on Decomposition of
Explosives. See under Decomposition of Explo-
sives in Vol 3, D23-L to D25-R

Pressure Measurements in Closed Bombs and
Weapons. See under Closed Bomb (or Vessel)
and Instruments for Measuring Pressures De-
veloped by Explosives or Propellants in Vol 3,
C330-L to C345-R

Primacord. See under Cord, Detonating; Cordeau Fuse or Detonating Fuse in Vol 3, C529-R to C531-L, and Detonating Cords or Detonating Fuses in Vol 3, D103-R to D107-L


Primary Explosives. See under Initiating Explosives in Vol 7, I105-L to I106-L

PRIMERS

Introduction – History.

The successful initiation of high energy material, which would include an entire variety of substances such as BlkPdr, smokeless or NC-type powder, pyrot or display powder, and HE material, is accomplished by the application of a small external stimulus, provided by a suitable source of energy.

This small initiating mechanism is available in a variety of forms and is generally referred to as a "primer" or a "detonator". The choice depends on the nature of the major high-energy material to be ignited. In most general terms, primers are used to effect the ignition and proper propagation of a burning process (Ref 13); eg, propell powder. Detonators serve an entirely different role and are intended to cause the functioning of a HE material (Ref 12). (Also see under "Detonators, Igniters, Primers and Other Initiating Devices Used for Nonmilitary and Military Purposes" in Vol 4, D733 ff)

Obviously, there are many combinations and variations of the use of primers and detonators. There are instances where primers are used to ignite detonators, the output of which is then used either to cause directly the operation of a main expl charge or to ignite a slow-burning delay column, followed by a detonator and an expl charge.

Figure 1 represents the difference in the two sequences of events (Ref 13)

High-energy materials such as BlkPdr and a wide variety of pyrots (truly "fireworks") have been known since before Christ; and, consequently, some primitive form of initiation for these was utilized.

It is remarkable that little is known about the development of the art of initiation until the invention of the first modern primers by Forsyth in 1807 (Ref 2). His formula was based on a mixt containing 70.6 parts of K chlorate, 11.8 parts of charcoal, and 17.6 parts of sulfur. It is equally remarkable that modern primers are very much the same as the early ones designed by Forsyth and that the mixts still remain a heterogeneous group of granular substances, capable of taking fire when struck.

The development of the first HE, NG, by Sobrero in 1846 and the later successful development of the means for utilizing NG as a practical expl by Nobel prompted invention of more efficient methods of initiating these HE's (Ref 6). It remained for Nobel to accomplish this task; and from this point on, the expl community, both commercial and military, would witness an ever-expanding family of initiating devices, beginning with Forsyth's early primer and extending to the highly sophisticated exploding bridgewire initiators.

![Schematic Representation of Explosive Trains](image-url)
These bridgewire devices are relatively safe from initiation by direct application of heat and external mechanical influences or from most electrical inputs. They are designed for highly specialized electrical impulses (Ref 13).

MECHANICAL INITIATORS
PERCUSSION PRIMERS, STAB DETONATORS, AND FRICTION PRIMERS

Although it is evident that initiators represent a broad spectrum of items and designs, both percussion and electric, the contents of this treatise will deal only with three selected types of percussion items; i.e., percussion primers, stab primers and/or detonators, and friction primers.

Percussion Primers

Percussion primers are used for the ignition of propellant powder, thereby ejecting a projectile from a weapon. Thus, a relatively small percussion primer containing a small amount of sensitive priming mixt, upon being struck by a sufficient blow from a firing pin, causes ignition of the propellant. In small arms ammo, the output of the primer is of sufficient magnitude to ignite the propellant directly. In larger-caliber rounds, particularly artillery rounds, an igniter or booster material (usually BlkPdr) is used to amplify the primer; and it is then the burning of the booster material which effects proper ignition of the propellant (Ref 6).

Percussion primers (also referred to as "caps" by the Brit) are either rimfire or centerfire (Ref 20). The use of rimfire priming is restricted to 0.22 cal ammo, which is almost exclusively commercial for sporting ammo, even though it is utilized to a minor extent by the military for training purposes. Rimfire priming is, in effect, an integral part of the small cartridge case.

Centerfire ammo, as the name implies, contains a primer (which is either a separately manufd piece or a partially completed item), located centrally in the head of the cartridge case.

There are four different types of percussion primers; and these are recognized by name as Boxer, Berdan, Bloehm, and Battery Cup. These centerfire primers and the rimfire type are shown in Fig 2.

Here are brief descriptions of these percussion primers. The Boxer primer consists of a metallic cup and anvil (both made from brass alloy: 70/30; Cu/Zn). Compressed priming mixt is contained between the cup and anvil. This primer is separately manufd and then inserted into a cavity in the base or "head" of the cartridge case. This cavity is commonly known as the "primer pocket". Neither Berdan nor Bloehm primers (which, incidentally, are seldom used in the USA, either for military or commercial ammo) contain anvils and are not complete until inserted into the cartridge cases. With the Berdan primer, the primer cup is charged with mixt and covered with protective foiling paper. The anvil is an integral part of the cartridge case, being formed in its original position in the base of the primer pocket.

The Bloehm primer is a slight variation of the Berdan type. The anvil is not an integral part of the cartridge case, but takes the form of a "spade" which is inserted into the centrally located primer vent in the cartridge case, after which the charged cup is inserted.

The primary mixt widely used by the US Army for small arms ammo in the early period of 1900 was based on Mercury Fulminate (MF) and is believed to be of Austrian origin (Ref 2). The most widely used formula is reported to have been as follows:

<table>
<thead>
<tr>
<th>Early (1900) US Army Priming Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury Fulminate</td>
</tr>
<tr>
<td>Potassium Chlorate</td>
</tr>
<tr>
<td>Antimony Sulfide</td>
</tr>
<tr>
<td>Powdered Glass</td>
</tr>
<tr>
<td>Gelatin Glue</td>
</tr>
</tbody>
</table>

Some time later, circa 1917, the US Army changed to a non-mercuric formula, which eventually was known as FA70 (Ref 20) (the "FA" signifying Frankford Arsenal)

FA70

| Potassium Chlorate                    | 53.0% |
| Antimony Sulfide                      | 17.0% |
| Lead Thiocyanate                      | 25.0% |
| TNT                                   | 5.0%  |

It is interesting to note that, from the time of the adoption of FA70, its use was continued as the standard mixt for cal .30 and cal .45 primers all thru WWII. A variation of FA70, known as FA90, was used in cal .50 (Ref 20).
Fig 2 Various Types of Percussion Primers
FA90
 Potassium Chlorate  53.0%
 Lead Thiocyanate  25.0%
 Antimony Sulfide  12.0%
 PETN  10.0%

Except for special application, especially primers intended for use in high-temp environments, K chlorate priming mixtures have been abandoned. The main reason for this change is that K chlorate primers are corrosive. After firing, hygroscopic K chloride, resulting from the decompr of the K chlorate, is deposited in the gun barrel. This causes immediate and extensive rusting of the barrel.

Many types of non-mercuric, non-chlorate priming compn have been investigated for use in small arms ammo. Despite the many years of study and testing of many mixes, Lead Stypheate (LST) compn, originally conceived by Rathburg in 1926 (Ref 1), were adopted by the US Army in 1948. Initially, small arms LST primers were purchased from commercial vendors, while the US Army proceeded to develop a standardized mix. This was accomplished in the formulation of FA956 mixt, which is used in all military ammo today. It is similar to the mixt used by commercial vendors for sporting ammo (Ref 20)

FA956
 Lead Stypheate, Normal  37.0±5%
 Tetracene  4.0±1%
 Barium Nitrate  32.0±5%
 Antimony Sulfide  15.0±2%
 Aluminum Powder  7.0±1%
 PETN  5.0±1%
 Gum Arabic  0.2% *

* 105ml of 1% soln used per 3500g of priming mixt

A review of the vast amt of work performed in the field of percussion primers reveals what is essentially an empirical approach to the development of both primer designs and priming mixts.

It is recognized that a percussion primer must perform two vital functions: (1) it must "fire", "ignite", or otherwise function when provided with the proper mechanical stimulus — a firing pin (with optimum contour to its striking end); and (2) it must perform its other function by which the "flame", "fire", or "output" will ignite the propint properly so as to provide the projectile with the specified velocity and within a specified range of gun chamber pressures; i.e., proper ballistic performance.

In order to fire reliably in a gun or other weapon device, a percussion primer must possess impact sensitivity which is in consonance with the mechanical energy delivered by the firing pin. In all cases, a factor of safety is built into the system in such a manner that the firing pin energy usually exceeds the max energy requirement of the primer by approx 20%.

In small arms percussion guns, the firing pin energy has been detd by having the firing pin impinge on a standard Cu cylinder inserted in the primer pocket. A variation of this technique is the use of "dummy primers", loaded with an inert mixt, the consistency and resistance to crushing thought to be more related to the actual firing process of the primer vis-a-vis the impact of the firing pin (Refs 2 & 20). In either case, the indentations produced are measured and compared to values produced in a "sensitivity drop-test machine". With a knowledge of the sensitivity of live primers and the use of a standard drop-test machine, the following relationships are established: (a) height of drop (inches) vs indentation (inches); and (b) height of drop vs percentage of firing (ie, sensitivity data). From this, the relationship between indent and sensitivity for any specified primer can be obtained. It is an easy step to add a factor of safety, which the designer must decide upon, and then specify the minimum indents that the firing pin of the gun must produce for high reliability of firing (Refs 3 & 20).

The sensitivity of a primer for a given firing pin/weapon system is then designed into the primer by the proper choice of the thickness of the base of the primer cup, the point radius of the anvil, and the degree of compression of the mixt between the anvil and the cup. This is controlled by the degree to which the anvil is compressed into the cup during manuf of the primer. In addition, some influence or further compression can be achieved when the primer is inserted into the cartridge case and crimped. This latter effect is minimal with the LST mixts (as compared to FA70 or FA90), and is further minimized by the use of flat-bottomed primer cups.

The choice of an available primer for a cartridge is dependent on the energy available in
the firing-pin system of the weapon (which can be altered within limits by changing the strength of the firing spring), and by the output required to efficiently ignite the propellant (Ref 3).

The output of a primer includes hot gases, hot particles, a pressure pulse (which, in some cases, may be a strong shock), and thermal radiation (Refs 6, 12 & 13). Some of the aspects of primer output which have been measured as a means of characterization include the following: (a) vol of gas emitted; (b) the impulse imparted to a column of Hg by the pressure pulse; (c) the light impulse as measured by a photocell; (d) the temp rise of a thermocouple in the stream of output gases and particles; (e) the ionic conduction between a pair of probes exposed to the output; (f) the pressure rise in a chamber in which the output is confined; (g) the propagation of the air shock; and (h) the “hangfire”, namely, the time lapse between supply of mechanical energy to the primer and the initial primer output and flame duration.

Some of the brisant primers emit pressure pulses of sufficient magnitude to give measurable results in either the sand test or the Pb-disc test. Although many of these quantities are related to some aspects of primer performance, insofar as output is concerned, no general quantitative relationship of overall value has been developed which can be used as a means of acceptance.

Primers are designed for specific applications, and the mixts chosen are largely based on precedent. Speaking very broadly, it can be said that the output must be characterized so that both gaseous products and hot particles are produced, both assuming important roles in ignition. The effectiveness of the gaseous products increases directly with temp and pressure; and, since pressure is related inversely to the enclosed vol, an increase in this vol or a venting of the system may call for primers of greater output.

It has been shown exptly that the heat of an enclosed body of gas is distributed quite uniformly over the surface to which it is exposed (Ref 4). Thus, the insertion of baffles or the introduction of irregularities which increase the total surface (both inert and reactive) exposed to the primer gases may necessitate the use of a primer with more output energy. Hot par-

ticles of solids or globules of liqs are very effective in the ignition of materials with high thermal diffusivities (such as those contg appreciable proportions of metal) or of those whose melting points are well below their ignition temps. Hot particles and globules establish a number of reaction nuclei, rather than burning along a uniform surface. This action may be undesirable in propellant grains designed for selected burning rate. Where the particles or globules are large or penetrate too deeply into the propellant, serious problems may result. One very dangerous effect would be over-ignition of the propellant, resulting in an extremely sharp rise in chamber pressure. This could be of sufficient magnitude to cause swelling or even rupture of the cartridge case and subsequent damage to the gun mechanism (Ref 20).

The blast effects of pressure pulse and accompanying gas movement are capable of producing both positive and negative effects. Although they result in more rapid heat transfer between gases and solid materials which are to be ignited, they may also extinguish the flame by moving the hot, gaseous products from contact with the individual propellant grains (ie, individual particles of propellant).

Shock waves from primers, quite often referred to as “brisance” or the “brisant effect”, may cause rupture of propellant grains (Refs 19 & 20). This effect is accentuated at low temps, at which condition the NC grains become more brittle and subject to fracture. This effectively results in the burning of much smaller propellant particles, radically increasing the burning rate. This then produces very high gun chamber pressures, which have been known to cause guns to expid.

The reproducibility of the time of a delay element is related to the reproducibility of the primer used for initiation. The times of short obturated delay elements are very sensitive to variation in primer output (Refs 7 & 12). Although primers of this type have been additionally tested for blast and gas vol, some opinions have held that, provided the priming mixt is maintained within the prescribed limits, the output is a mere reflection of the pellet wt.

When a percussion primer is used to drive a firing pin to cause a series of events to occur, an important aspect of primer output is the moment-
...um it is capable of imparting to a firing pin. Where the output gases are reasonably well contained, the impulse is measured in the gas vol and impulse apparatus. Again, this seems to be another cogent argument for the necessity of maintaining primer pellet wt within very close tolerances.

In dealing within the confines of a standard priming mixt which has been used successfully in other cartridges, the kind of primer required for a different application requires essentially the solution of two problem areas: (a) the design of the primer in terms of mechanical aspects so that it will properly interface with the weapon; this would include but not necessarily be limited to a knowledge of the kinematics of the firing rate of the weapon, etc; and (b) the amount of priming mixt required for proper ignition and burning to obtain specified internal and external ballistic characteristics.

Generally speaking, the ordnance designer works backwards from the target. Target effects translate to projectile parameters; i.e., mass, diameter, ballistic coefficient, and velocity. Exterior ballistics dictate interior ballistics, and the end result is a choice of the primer-propint combination. With the propint type and charge calc'd, it is possible, based on precedent, to make a reasonable estimate of the amt of standard type of LS mixt, preferably FA956, required (Ref 20).

Working around this estimated pellet wt, a series of primers with different but known pellet wts are prepared. In a well-conducted investigation, a group of five different lots of primers, with 30 primers to a lot and the exact pellet wt of each primer recorded, are assembled into complete cartridges with the same charge of propint. These rounds are then fired at +70°F, +165°F, and -60°F, single shot in a test weapon, recording velocity, pressure, and barrel time (the time interval between beginning of pressure rise due to propint ignition to exit of the projectile from the gun barrel). The barrel time versus pellet wt is plotted for each temp, and curves similar to that in Fig 3 are obtained.

![Diagram of Tolerable Range of Pellet Weight vs Barrel Time in Milliseconds](image-url)
Examination of these curves will show a flat portion, where further increase in pellet wt causes little or no change in barrel time. This portion of the curve is examined judiciously; and a pellet weight is chosen which, with the normal variations that can be expected in the primer manuf, will have minimal effect on barrel time.

Sensitivity testing of primers (Refs 3 & 15) is conducted with the primers inserted into the specified cartridge case in which they are to be used. The primer is inserted into the primer pocket of the cartridge case so that the surface of the primer cup, when measured from the center of the primer, is within the tolerance specified on the applicable cartridge drawing. The test is performed in accordance with the complete run-down method described in TECP 700-700, Volume III; AMCR 717-505, Volumes 3 and 5; or AMSMU-P-715-501 FA1, as applicable.

The sensitivity testing is conducted using a standardized app, which is known as “Fixture, Testing, Primer Sensitivity”, US Army Ordnance Department Drawing No 81-3-44. Briefly, this is a very sturdy iron stand which is easily adjusted and leveled, and contains a lower base where the test cartridges are inserted in suitable holding dies, over which is a firing pin holder in a swing-over latch. This secures the firing pin directly over the primer. A vertical member, with suitable graduations in inches, allows a solenoid to be fixed at variable heights and holds the steel ball which, upon release, impinges directly on the vertical firing pin. The mass of the ball used depends on the primer to be tested, and the mass is specified in the appropriate primer specification. These steel ball bearings are usually used in 1-, 2-, 4-, 8-, or 16-ounce wts.

The actual test procedure generally prescribes a sample of 400 primed cases. Fifty sample primed cases are tested at each height (where the drop-height is measured as the distance from the bottom of the ball to the top of the firing pin). The number of primers that fire — or fail to fire — is recorded, and this procedure is repeated at successively increasing heights of fifty primed cases at each height until a height is reached at which all primers tested fail to fire.

The raw data of fires and “no-fires” is translated into meaningful sensitivity data by use of a calcn sheet shown in Table 1.

The data thus calc'd, $H$, the height at which 50% of the sample fired and $\sigma$, the standard deviation, can then be used to calc the height at which all primers will be expected to fire at a chosen confidence level:

$H + 5\sigma = $ All Fire Height (height at which not more than 3 out of 10,000,000 would misfire)

and also to determine the height at which all will misfire:

$H - 2\sigma = $ All Misfire Height (height at which not more than 1 out of 50 will fire)

The skewness is calc'd to determine whether or not the particular lot of primers under test manifest a normal distribution. As a general rule, skewness is often recognized at the high drop heights, where the sensitivity curve tends to lengthen. This tendency may be observed in the study of exptl mixts or designs. When observed, lowering of the value to obtain normal distribution can be achieved by adjustment of the formula of the priming mixt or a change in metallic components. Standard primers which have long and successful records of manuf and sensitivity normally exhibit low and acceptable skewness values (Ref 3).

Currently, the official US Army category of small arms ammo comprises cartridges ranging from 5.56mm up to and including 30mm. The following (Table 2) is a list of these primers and the matching US Armament Command Drawings applicable to these percussion primers. (It should be noted that this entire family of primers requires the use of “stphnate” priming compns. Further definition of “stphnate” means normal LSf (Ref 11) and, in most cases, FA956 primer compn).
### Table 1
Calculation Sheet for Primer Sensitivity and Skewness

<table>
<thead>
<tr>
<th>$H = H_t$</th>
<th>$p_i$ = Fraction Misfiring</th>
<th>$k_i$ = Variance Factor</th>
<th>$k_i p_i$ = Variance Factor times Fraction Misfiring</th>
<th>$s_i$ = Skewness Factor</th>
<th>$s_i p_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td></td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>19</td>
<td></td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>37</td>
<td></td>
<td>259</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>61</td>
<td></td>
<td>547</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>127</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>169</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>217</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>271</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>331</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>397</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>469</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>547</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\sum p_i = \Sigma k_i p_i = \Sigma s_i p_i =$

$H_{100\% + .5} = -\left(\sum p_i\right)^2$

$H = \sigma^2$

$H_{100\% = 1st \text{ ht}}$ at which 100% misfire

$\mu_3 = \Sigma s_i p_i - 3 \Sigma k_i p_i \Sigma p_i + 2 (\Sigma p_i)^3$

$\alpha_3 = \mu_3 / \sigma^3$ = skewness value

### Table 2
US Army Armament Command Drawings

- B8595819 - Primer (Styphnate) for Caliber .30 Match
- C7645332 - Primer (Styphnate) for Caliber .30 and Caliber .30 Blank
- B6200959 - Primer (Styphnate) for Caliber .30 Carbine
- C11751131 - Primer (Styphnate) for Caliber .30 Carbine
- B10534279 - Primer (Styphnate) for 5.56mm
- B8594094 - Primer (Styphnate) for 7.62 Match

- B10522621 - Primer (Styphnate) for 7.62mm, 7.62mm Blank, 7.62mm Grenade, 7.62mm Match, and Caliber .30
- B1053489 - Primer (Styphnate) for 7.62 Match, 7.62mm Blank, Caliber .30, and Caliber .30 Match
- B7645336 - Primer (Styphnate) for Caliber .45 and Caliber .45 Blank
- B7645339 - Primer (Styphnate) for Caliber .50
Since the quantity of small arms ammo manufactured and expended is extremely high, greater emphasis has been placed on an explanation of the primers used in these rounds. However, this in no way is intended to diminish the importance of additional types of percussion primers which find wide use in artillery ammo (Table 3).

Table 3
Percussion Primers Used in Artillery Ammunition

<table>
<thead>
<tr>
<th>Primer</th>
<th>Command Drawing</th>
<th>For Use In</th>
</tr>
</thead>
<tbody>
<tr>
<td>M36A2</td>
<td>D7259094</td>
<td>20mm Percussion Ammo</td>
</tr>
<tr>
<td>M61*</td>
<td>8831157</td>
<td>BkPdr Tubes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Number of Artillery Rounds</td>
</tr>
<tr>
<td>M29A1**</td>
<td>8798312</td>
<td>Fuses</td>
</tr>
<tr>
<td>M42***</td>
<td>See McDonnell</td>
<td>Fuses</td>
</tr>
<tr>
<td></td>
<td>Aircraft Company</td>
<td>Report #MDCA0514 of 30 June 1970</td>
</tr>
</tbody>
</table>

* Loaded with FA70 Composition
** Loaded with PA101; contains basic Lead Styphnate
*** Loaded with either FA70 or Lead Styphnate compns

The firing pin mechanisms used in both small arms weapons and artillery guns produce firing pin energies of considerable magnitude. As a matter of illustration, the spring-actuated firing pin of the M-14 rifle has a striking energy of at least 100 inch-ounces; whereas, the primers for these 7.62mm cartridges require 60 inch-ounces. This favorable situation results from the fact that no excessive restriction is placed on the weight, volume, or geometry of the firing mechanism. Consequently, the primers used in these weapons are considered to possess a normal degree of sensitivity. This allows the ordnance to be handled safely, yet insures reliable performance in the weapon (Refs 2, 5 & 9).

In mechanical fuses, where percussion primers are required, it seems fairly obvious that space requirements impose limits on the size of spring mechanisms or other physical modes of causing firing pins to move. The result is that, for fuses and other applications of this type, it becomes necessary to use primers of greatly increased sensitivity (Refs 6 & 8). This condition is illustrated with the M29A1 primer which is required to fire with an applied energy of 16 inch-ounces. This increased sensitivity is achieved by the use of thinner primer cup metal of softer alloy. Sensitivity can be further enhanced by the use of more sensitive priming mix (Refs 2, 6 & 20).

Table 4 shows the approved and standardized priming mixtures which possess greater sensitivity than FA70, FA90, or FA956, previously listed (Refs 8, 12, 13, 17 & 20).

<table>
<thead>
<tr>
<th>High-Temperature-Resistant Percussion Primers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Until the USA became seriously involved with</td>
</tr>
<tr>
<td>the space program in 1957, little emphasis</td>
</tr>
<tr>
<td>was placed on the performance of ordnance,</td>
</tr>
<tr>
<td>particularly high energy materials, after</td>
</tr>
<tr>
<td>exposure to significant periods of high temps.</td>
</tr>
<tr>
<td>Firing of ammo at -65°F and +165°F had been a</td>
</tr>
<tr>
<td>routine procedure in research and developmental phases, but no requirements had ever been enunciated for performance criteria at higher than +165°F or for prolonged exposure to this or even higher temps (Ref 9).</td>
</tr>
</tbody>
</table>

The motivation to develop high-temp-resistant primers is well documented by McDonnell Aircraft Company (Ref 15), based on early work by

Table 4
Standardized Priming Mixtures

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>PA100</th>
<th>PA101</th>
<th>793</th>
<th>NOL160</th>
<th>NOL130</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Styphnate, Basic</td>
<td>53%</td>
<td>39%</td>
<td>60%</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Lead Styphnate, Normal</td>
<td>38%</td>
<td>39%</td>
<td>22%</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>Barium Nitrate</td>
<td>2%</td>
<td>2%</td>
<td>5%</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>Lead Azide</td>
<td>11%</td>
<td>14%</td>
<td>10%</td>
<td>15%</td>
<td>10%</td>
</tr>
</tbody>
</table>
the Frankford Arsenal (Ref 9) and Remington Arms Company, Inc (Ref 14). It is important
to note that these primers were required for
propellant-actuated devices (PAD) used in mili-
tary aircraft to perform a variety of functions.
The most important illustration of this type of
device is the pilot ejection system, which in-
cludes many propellant devices, each activated by
percussion primers. The entire system culmi-
nates in the ejection of the pilot from the air-

It was found that the primers used in these
systems, which contained FA70 priming mixt,
were subject to solar radiation in closed areas
(in some locations in the aircraft), which pro-
duced temps of up to +235°F. In addition, it
was predicted that certain devices would be
exposed to temps estimated at +400°F. As a
result of the consideration of these factors, a
goal of successful functioning after 2000 hours
at 400°F was established

The development of a reliable high-temp-
resistant primer was a problem of considerable
challenge and technical effort. It was found that
none of the available expl-type priming mixts
would survive. Eventually, mixts based on the
use of K chloride evolved. Two high-temp mixts
were developed as shown below (Refs 14 & 20)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>G-11</th>
<th>G-16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Chlorate</td>
<td>53%</td>
<td>53%</td>
</tr>
<tr>
<td>Antimony Trisulfide</td>
<td>25%</td>
<td>30%</td>
</tr>
<tr>
<td>Calcium Silicide</td>
<td>12%</td>
<td>17%</td>
</tr>
<tr>
<td>TACOT **</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>

* The percentages shown are by wt
** TACOT is the trade name for a duPont high-
temp-resistant secondary expl

Mixture G-11 has been demonstrated to be
the more preferable of the two mixts and has
been manufd in three different types for various
applications. This is a relatively brisant primer, will withstand 400°F for prolonged periods,
and will continue to operate. Depending on the
metal components used (cups and anvils), the
energy to fire will vary as follows (Ref 15):

<table>
<thead>
<tr>
<th>Primer</th>
<th>Energy Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>44-G11</td>
<td>90 inch-ounces</td>
</tr>
<tr>
<td>49-G11</td>
<td>85 inch-ounces</td>
</tr>
<tr>
<td>72-G11</td>
<td>100 inch-ounces</td>
</tr>
</tbody>
</table>

Stab Detonators

It is becoming increasingly clear that the pre-
ponderant amt of modern ordnance requiring the
initiation of HE charges utilize electric initiation.
However, there still remains a continued require-
ment for the use of percussion initiation. The use
and description of sensitive artillery primers, eg,
M29A1, etc, to accomplish this has previously
been discussed

In instances where the expl is to be detonated
without a primer and whose output will not re-
liably initiate secondary HE charges, the initiator
takes the form of a stab detonator (Refs 8, 12
& 13), a diagram of which is shown in Fig 4

As shown in Fig 4, the stab detonator is a
small, sensitive component which is capable of
reliably initiating high-order detonation in the
next HE element in the expl train. It differs
from the primer in that its output will initiate
reliably secondary HE charges

Stab detonators are made in the form of
cylindrical cups of Al, stainless steel, Cu, or
gilding metal. The open end is sealed with a
closing disc of metal or of paper over which the
end of the cup is crimped

Whereas primers contain a single heterogene-
ous expl charge of priming mixt, detonators
and especially stab detonators contain three
charges, primary, intermediate, and base, al-
though sometimes two or three are combined.
The primary charge is near the input or accep-
tor end and the base charge is near the output end.
With stab detonators, the percussion sensitivity
is a function of the type of priming compn used
(see Table 4), the loading pressure exerted on
the mixt during manuf, and the thickness and
rigidity of the metal at the input end. In addition — and of vital importance — is the configuration of the striking end of the firing pin, the standard design of which is shown in Figure 5.

The functioning of a stab detonator involves the conversion of mechanical energy into concentrated heat, with the energy necessary being nearly proportional to the amount of material (priming mixt) which is heated (Ref 4). The standard firing pin is a truncated cone. It has been found that the less sensitive the priming mixt, the larger the optimum diameter of the flat. It has also been determined, both by experience and test, that the most compact shape for a cylinder is one whose length is equal to its diameter. Thus, as the energy required for initiation is increased, it is advantageous to distribute it over a large enough area to limit the effective length to nearly its diameter. The flat diameter as shown serves the standard priming mixts in use. Both steel and Al alloy firing pins are used, but Al results in a significant but not serious decrease in sensitivity. The effect of eccentricity of the firing pin is such as to cause a decrease in sensitivity.

Since stab detonators contain no restraining anvil as do percussion primers, the resistance to penetration of the firing pin becomes quite important. This is the role of compression or density of the mixt. With higher density, the kinetic energy of the firing pin is dissipated over a shorter distance, so that a smaller quantity of expl is heated to a higher temp (Table 5).

**Table 5**

<table>
<thead>
<tr>
<th>Loading Pressure (1000psi)</th>
<th>Drop Test Height (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.31</td>
</tr>
<tr>
<td>25</td>
<td>0.91</td>
</tr>
<tr>
<td>40</td>
<td>0.77</td>
</tr>
<tr>
<td>60</td>
<td>0.68</td>
</tr>
<tr>
<td>80</td>
<td>0.57</td>
</tr>
</tbody>
</table>

* NOL priming mix in MARK 102 cups; 2-ounce ball.

Since the resistance of solids to deformation does not change very much with moderate changes of deformation rate, the power dissipation by the displacement of compressed priming mixt by a firing pin is nearly proportionate to its velocity (Ref 19).

Pb Azide (LA), which is the most important expl used in detonators (Ref 11), although extremely sensitive to shock, heat, and friction, is not sufficiently sensitive to stab action to insure 100% reliability in firing from the stab action. Consequently, the priming mixt is used as a first-fire layer in these units. RDX (cyclotrimethylenetritramine), also known as Cyclonite, is contained as the output charge of the typical stab detonator. Its output results in a detonation of other expls (Ref 11).

The selection of a stab detonator for a specific application requires a consideration of both input and output (Ref 7). The situation exactly duplicates the problems encountered in the selection of a percussion primer. However, as previously discussed, the end purpose of a detonator is different: the input energies are significantly lower, and the output is intended to initiate a high expl. In addition to the main criteria, consideration must also be given to size, weight, cost, and reliability.

When designing a stab detonator, the engineer will select the firing pin so that the entire initiation mechanism is under control. This permits close coordination with other systems designers involved in the weapon development, and thus ensures that the stab detonator will receive the proper stimulus.
The output of a stab detonator is a detonation. Unfortunately, available output data are more non-specific than input data so that firm, quant choices of output are difficult to make. Consequently, comprehensive testing is usually required (Refs 6 & 12).

In addition to the type of output, the functioning time of the detonator, which is the interval from delivery of the input to the stab detonator until the output of the initiator is realized, is of considerable importance. Where fast initiation is required, the use of LA is essential and, in addition to being used as the intermediate charge, is sometimes incorporated in the initial priming charge in minor percentages to decrease the operation time of the LST mix.

The sensitivity requirements of stab detonators, like percussion primers, are specified in terms of wt and height of a falling ball, measured in a standard drop-test machine (Refs 8, 12 & 13). The actual test detonators are contained in an enclosed but vented housing. The actual sensitivity can be determined by using the complete rundown method, which has been described under "Percussion Primers". Although requiring a relatively large sample, it provides an excellent assessment of the distribution of the underlying population. The data are treated in the same manner as previously described, which permits the calculation of the all-fire and all-misfire heights or energies.

In the case where the number of samples is more limited, the staircase or Brueton test is applied. This is one in which a predetermined set of steps in the magnitude of the initiating stimulus is established before starting and in which the magnitude for each trial is determined by results of previous trials. In the Brueton test, the magnitude of stimulus used in each trial is determined by the result obtained in the immediately preceding trial. If the preceding trial resulted in a misfire, the stimulus to be used in the present trial is one step higher than that in the previous trial. If it fired, the stimulus of the present trial should be of a magnitude one step lower. The test is continued in this manner for a predetermined number of trials.

The validity of the results of this procedure depends on whether the assumption is valid that the steps are of uniform size in a system in which the frequency of explns is normally distributed.

The Brueton test is most applicable to systems for which extensive tests have established the nature of a generic normalizing function. Unfortunately, it is often applied to systems for which it is not economically feasible to carry on such a program. The Brueton expln technique is often used as a convenient means for the collection of data in situations where the assumption of normality is known to be false and where it is intended to use other methods of analysis.

An objection which has been raised to this practice is that the strong tendency of the Brueton technique to concentrate testing near the 50% point reduces the value of the data in estimating the nature and deviation of the distribution. However, it is pointed out, the sample sizes available are usually so small that a reasonable estimate of the mean and a rough guess of the deviation is the most which can be expected.

The output of detonators, regardless of the mode of initiation, is intended to induce detonation in a subsequent charge. The two features of output which are useful for this purpose are the shock wave it emits and the high velocity of its case (fragments). Although it is possible to imagine detonator designs which are effective in inducing detonation without detonating themselves, the output effectiveness of detonators is directly related to the quantity of the explosive which detonates, and to the strength of this detonation. These quantities are somewhat less predictable than in most other components because the transitions from burning to detonation and from low-order to high-order detonation take place in the detonator. These transitions may require anything from one hundredth of an inch to the whole length of the detonator, depending upon such factors as loading density, compn, particle size, confinement, and column diameter. Recent improvements in LA production have resulted in materials in which these transitions require so little expln that the output of a detonator can be predicted with a fair degree of confidence (Ref 17). The effective output of a stab detonator includes factors of pressure, duration, and area over which the pressure acts.

Detonator output is difficult to characterize except in terms of the characteristics of a subsequent charge. This is to be expected because the transmission of detonation involves the interaction of quantities associated with the acceptor.
as well as with the donor. Output is measured by means of gap or barrier tests, sand test, Cu block test, Pb disc test, steel plate dent test, Hopkinson bar test, and in terms of the air shock produced. These tests are described in various publications (Military Standards 316, 317 & 320).

Both the Pb disc test and the steel dent test are of particular significance to stab detonators. As a matter of illustration, the steel dent test (Ref 10) consists of firing a detonator in direct end-on contact with a steel block. The depth of the dent produced is a measure of output. The depth, or better, the volume of the dent correlates well with initiation effectiveness. The low-rate detonation, which crushes nearly as much sand as high-order detonation, makes no dent in a steel plate. It has been demonstrated that the depth of the dent is proportionate to the excess of pressure over the yield strength of the steel of the dent block, integrated over the volume of the detonation head. It has been found that a detonator of 0.190-inch diameter or larger, which produces a dent 0.010 of an inch deep in a mild steel block, will initiate a load of Tetryl or RDX under favorable conditions. Specification requirements for detonators to be used in fuses are usually at least 0.015 to 0.020 inch in depth, and many produce dents up to 0.060 inch deep.

Stab detonators, as a subclass of initiators, in general are loaded by pressing powdered expls into the cup. Although most initiators are loaded at between 10,000 and 20,000 psi, stab priming mixts are pressed at between 30,000 and 80,000 psi. This increment is loaded first, since the priming mixt is the most vulnerable to moisture and other atm gases; consequently, it is farthest from the crimped end in a coined-bottom cup. The intermediate charge of the stab detonator is LA, which is used exclusively in this application due to its demonstrated superiority over other expls. Although most detonators have previously used dextrinated LA, the variation in performance in the growth of detonation has caused a preference of other forms such as RD1333, a development of Brit origin (Ref 13).

The base charge of stab detonators had usually been Tetryl but present designs use RDX. The total energy released by a stab detonator is the sum of the heat of detonation and the quantities of the various expls used. Of this energy, only that from the expl which detonates high-order is effective initiation output obtained. In general, this includes the base charge and part of the intermediate charge. The azide which actually detonates must be sufficient to initiate the base charge. In current detonator designs, this is assured by the use of at least 100 milligrams of LA. It is common practice to require 0.10-inch minimum column heights. Although the use of RD1333 (Ref 12) permits smaller quantities of this type of LA, sufficient data has not been accumulated to provide reliable minimum quantities.

A final and important factor in the output of a stab detonator or, as a matter of fact, any type of detonator, is the confinement afforded by the containing structure. This is difficult to describe in quant terms because different properties of the confining structure are involved in the promotion of detonation growth and in increase of the output of stable detonation; the confinement provided by surrounding fuse structures as well as that of the detonator itself can contribute significantly to the effective output of a detonator. In the detonation process, tightness is the most important factor in the early stages; whereas, as the growth continues, the strength of the container becomes important. As a stable rate of detonation is achieved, the pressure exceeds the bursting strength of any normal type of container and confinement is chiefly a matter of inertia.

A list of some of the more commonly used stab detonators, together with a short compilation of some important factors for each, is shown in Table 6.
<table>
<thead>
<tr>
<th>Lead Side (inches)</th>
<th>Lead Side (inches)</th>
<th>PA # 100</th>
<th>CM</th>
<th>2</th>
<th>6</th>
<th>106</th>
<th>102</th>
<th>115</th>
<th>108</th>
<th>1797</th>
<th>9.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>180</td>
<td>NO! 130</td>
<td>AL</td>
<td>2</td>
<td>4</td>
<td>200</td>
<td>192</td>
<td>115</td>
<td>115</td>
<td>192</td>
<td>115</td>
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<tr>
<td>200</td>
<td></td>
<td>NO! 85</td>
<td>SS</td>
<td>1</td>
<td>4</td>
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<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>7.5</td>
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<tr>
<td></td>
<td></td>
<td>PA! 350</td>
<td>SS</td>
<td>2</td>
<td>2</td>
<td>245</td>
<td>241</td>
<td>241</td>
<td>241</td>
<td>241</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PA! 365</td>
<td>CM</td>
<td>3</td>
<td>4</td>
<td>302</td>
<td>302</td>
<td>115</td>
<td>115</td>
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<td>5.1</td>
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<td></td>
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<td>CM</td>
<td>3</td>
<td>4</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PA! 105</td>
<td>CM</td>
<td>3</td>
<td>4</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>5.1</td>
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<tr>
<td></td>
<td></td>
<td>PA! 110</td>
<td>CM</td>
<td>3</td>
<td>4</td>
<td>115</td>
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<td>115</td>
<td>115</td>
<td>115</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PA! 116</td>
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<td>4</td>
<td>15</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base Chg (MC)</th>
<th>Inner Chg (MC)</th>
<th>Primer Mix</th>
<th>Cup Mill</th>
<th>Hi O! Drop (inches)</th>
<th>Wt. of Ball (oz)</th>
<th>(max) Inches Length</th>
<th>(max) Inches Diameter</th>
<th>Primer No.</th>
<th>Item No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Stand Primer Data.
Friction Primers

The importance of frictional heating in the initiation of expls is a subject of considerable importance. The frictional sensitivity is directly involved in the handling hazards of all high-energy materials; and considerable attention has been directed toward gathering of frictional sensitivity data on almost all mil expls, in addition to an entire host of pyrotechnic mixts and certain proplnts (Refs 6 & 17).

Although a significant quantity of this information has been obtained, initiating devices operating on this principle and known as friction primers appear to be anachronous.

Friction primers are devices for the production of fire, where the mechanical stimulus is either a push or pull of a roughened rod or wire thru a pellet of priming compn. These were used for firing artillery in situations where the proplnt charge was loaded separately and not enclosed in a brass case, complete with ignition tube and percussion element (percussion primer). They have also been used by being cramped to the end of a Bickford fuse as a means of ignition. This latter system has been replaced by a mechanical fuse lighter which operates by first removing a safety pin and then pulling a handle back which compresses a spring with attached firing pin. At the end of the rearward stroke, the pin and spring are released, moving forward to strike a conventional percussion primer.

Friction primers have also been used for igniting flares which were then thrown overboard from aircraft. It would appear obvious that any application in which ordnance is manually ejected from aircraft would conjure up thoughts of WWI systems. In any event, the pull element of the primer was attached to the aircraft by a suitable length of twine or wire; and the mass of the falling flare pulled and then broke it off.

The mixts which were most favored for friction primers were as follows (Ref 6):

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>K Chlorate</td>
<td>67%</td>
<td>56.2%</td>
<td>44.6%</td>
</tr>
<tr>
<td>Sb Sulfide</td>
<td>33%</td>
<td>24.6%</td>
<td>44.6%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>—</td>
<td>9.0%</td>
<td>3.6%</td>
</tr>
<tr>
<td>Meal Powder</td>
<td>—</td>
<td>—</td>
<td>3.6%</td>
</tr>
<tr>
<td>Ground Glass</td>
<td>—</td>
<td>10.2%</td>
<td>3.6%</td>
</tr>
</tbody>
</table>

All ingredients were in the powdered form except in the Type 1 mixt, where half the K chloride is powdered and the other half is in granular form. Apparently, the first mixt was considered best; the sulfur contained in the second and third mixts served to increase sensitivity but compromised the storage life. Mixts of sulfur with K chlorate were subject to decomp in moist atm. Although efforts were made to decrease the decomp by the additional anti-acid agents, eg, Ca carbonate, trimethyamine, etc., and the use of high percentages (5%) of gum arabic, these mixts soon disappeared from the scene. This is in the same time frame in which the US Army abandoned the use of sulfur with K chlorate in percussion primers and adopted FA70, in which the sulfur was replaced by K thiocyanate.

What has been described so far constitutes only one half of the friction primer, ie, the main charge, contained in a cylindrical cup. Centrally located in the K chlorate mixt was a loop of braided wire, coated with red P (90%) and dried shellac (10%). Any mixt of red P with K chlorate was, and still is, very sensitive, hazardous, and unpredictable. There is ample reason to understand why friction primers were abandoned and replaced with spring-actuated firing pins to fire percussion primers and carry the sequence thru a suitable expl train.

Attempts to find any present application have not been fruitful. It is possible that, in the vast array of ordnance, some type of friction primer device may still be in use.

Written by T. Q. CICCONE


Prism or Prismatic Powder. See under Black Powder or Gunpowder in Vol 2, B167-R
Addnl Ref: Davis (1943), 41–42

PRODUCTS, DETONATION

Detonation is universally defined as a chemically supported shock wave. It is a cooperative process in which the shock wave activates an exothermic chem reaction and the chem reaction, in turn, supports the shock. The products generated in such detonation reactions are the subject of this article. A very cursory description of detonation products was given in Vol 4, D494-R. Below we will consider the main equilibria that control the compn of detonation products, and present examples of product compns calc’d theoretically as well as observed exptly.

Detonation Equilibria. Most of the commonly used expls are compns or mixts whose elemental compn consists of C, H, N, O. If the expl is reasonably oxygen-balanced (see Oxygen Balance in this Vol) then the detonation product compn is primarily detd by the water gas equilibrium:

\[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \]  

(1)

Note that there is no net change in the number of moles of gas in this equilibrium. Therefore, by Le Chatelier’s principle, this reaction will be independent of external pressure (ignoring second-order effects due to gas imperfections). Under these conditions the N of the expl will appear as N₂ in the detonation products.

For oxygen-rich expls NO will be produced according to the reaction

\[ \text{N}_2 + \text{O}_2 = 2\text{NO} \]  

(2)

This equilibrium is also independent of pressure.

In oxygen-poor expls the so-called soot reactions become important. These are:

\[ 2\text{CO} = \text{CO}_2 + \text{C}(s) \]  

(3)

\[ \text{CO} + \text{H}_2 = \text{H}_2\text{O} + \text{C}(s) \]  

(4)

Note that the right-hand terms of reactions (3) and (4) contain fewer moles of gas than their respective left-hand terms. Consequently increase in pressure will drive both these reactions to the right.

If the expls contain excess H the reactions

\[ \text{N}_2 + 3\text{H}_2 = 2\text{NH}_3 \]  

(5)

and

\[ \text{C}(s) + 2\text{H}_2 = \text{CH}_4 \]  

(6)

will also come into play, but will not influence product compn as much as reactions (1), (3) and (4). Reactions (5) and (6) as written are also favored by high pressure.

Except for O₃ (a product in oxygen-rich expls), equilibria (1) thru (6) account for all major detonation products of condensed CHNO expls. In gas detonations (ie, at low detonation pressures) such species as OH, H etc may also exist. In “experimental” measurements of detonation products (to be discussed later) HCN frequently appears as a minor product.

For expls containing halogens (X), there is some controversy about the form in which these appear in detonation products. Some theoretical calcns (Ref 2) indicate that halogenated expls produce CX₄. Exptl measurement (Ref 4),
however, suggest that the main product is HX and very little CX₄ is formed.

Metallized expls or expls containing metal salts produce metal oxides. For example, in aluminized expls the Al reacts with any available oxygen to form Al₂O₃.

Experience has shown that the oxygen distribution in the products of a metallized military explosive favors the formation of the metal oxide. Any remaining oxygen then forms steam with the H of the expl. If any oxygen is still available it forms CO₂, and any unreacted C atoms then show up as free carbon in the products. (Confinement of the expls favors the formation of CO₂ and C at the expense of CO.) In halogenated expls HX appears to be formed in preference to H₂O and H₂.

We have noted that an increase in pressure tends to shift all the above reactions, except (1) and (2), to the right. We will now show that an increase in temp shifts equilibrium (1) to the right, but rather mildly, whereas it shifts all the other equilibria strongly to the left. Thus for reactions (3) thru (6) to be important, the effect of pressure must override the effect of increasing temp.

The effect of temp on chemical equilibria is conventionally determined via the free energy function ΔG°/RT and the ideal equilibrium constant K. Table 1 gives the free energy function G°/RT for the important detonation products of CHNO expls. From these data ΔG°/(RT) can be obtained for different temps for the reactions of interest, and ideal equilibrium constants computed according to:

\[ \ln K = -\Delta G°/(RT) \]

where

- G° = standard state Gibbs free energy
- R = gas constant
- T = absolute temperature

### Table 1

<table>
<thead>
<tr>
<th>T, °K</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂O</th>
<th>H₂</th>
<th>C₅</th>
<th>NH₃</th>
<th>N₂</th>
<th>CH₄</th>
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<td>-20.20</td>
<td>-3.256</td>
<td>-32.83</td>
<td>-28.12</td>
<td>-34.70</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

From Table 1 and Eq (7) we obtain the following:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>K(_{1000°K})</th>
<th>K(_{1600°K})</th>
<th>K(_{3000°K})</th>
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<tbody>
<tr>
<td>(1)</td>
<td>0.70</td>
<td>2.97</td>
<td>7.24</td>
</tr>
<tr>
<td>(3)</td>
<td>0.58</td>
<td>2.9 \times 10^{-4}</td>
<td>1.2 \times 10^{-5}</td>
</tr>
<tr>
<td>(4)</td>
<td>0.40</td>
<td>1.1 \times 10^{-3}</td>
<td>8.6 \times 10^{-8}</td>
</tr>
<tr>
<td>(5)</td>
<td>8 \times 10^{-7}</td>
<td>3 \times 10^{-9}</td>
<td>3 \times 10^{-11}</td>
</tr>
<tr>
<td>(6)</td>
<td>0.097</td>
<td>-</td>
<td>6.1 \times 10^{-5}</td>
</tr>
</tbody>
</table>
These data show quite clearly that increasing temp (detonation temp is expected to be in the range of 2000–4000°K) does not favor the products of reactions (3) thru (6).

For nearly oxygen-balanced expls equilibrium (1) will dominate and control the compn of the detonation products. As already stated this equilibrium is expected to be independent of pressure if the gases behave ideally. But even for ideal gas behavior and an oxygen-balanced expl, no direct comparison can be made between theoretical detonation product calcs and observed products. This is so because measurements are made at temps much lower than detonation temps, and the products reequilibrate as the temp drops. Further complications arise because the reequilibration freezes at some rather high temp. This is a consequence of reaction rates. At temps below some frozen equilibrium temperature, $T_f$, reaction rates become so slow that for all practical purposes further reequilibration ceases even if the temp drops well below $T_f$.

To anticipate some of the results to be presented later, it is instructive to compute the equilibrium compn of PETN at 1600°K. PETN is nearly oxygen-balanced and as will be shown later its $T_f = 1600^\circ$K. The empirical formula for PETN is $C_5H_8N_4O_12$. Let X be the number of moles of $CO_2$ at equilibrium, and C, H, O the original gram atoms of carbon, hydrogen and oxygen respectively. Then from mass balance and Raoult’s law

\[
\frac{p_{CO}}{n_t} = \frac{P(C-X)}{P_t - P(X + Y)}
\]

\[
\frac{p_{CO_2}}{n_t} = \frac{PX}{P_t - P(X + Y)}
\]

\[
\frac{p_{H_2O}}{n_t} = \frac{P}{n_t} (O-C-X)
\]

\[
\frac{p_{H_2}}{n_t} = \frac{P}{n_t} (\frac{1}{2}H+O+X)
\]

where

- $n_t$ = total number of moles of gas at equilibrium
- $P$ = partial pressure
- $P_t$ = total pressure at equilibrium

The ideal equilibrium constant for reaction (1) is

\[
K = \frac{p_{CO}p_{H_2}O}{p_{CO_2}p_{H_2}} = \frac{(C-X)(O-C-X)}{X((\frac{1}{2}H+C-O+X)}
\]

\[
= \frac{(S-X)(2-X)}{X(X-3)}
\]

for PETN.

From Table 1, $K=2.97$ at $T=1600^\circ$K and $X=3.50=$ moles $CO_2$ per mole of PETN; $C-X=1.50=$ moles CO per mole of PETN; $O-C-X=3.50=$ moles $H_2O$ per mole of PETN; $\frac{1}{2}H+C-O+X=0.50=$ moles $H_2$ per mole of PETN; $N/2=2.00=$ moles $N_2$ per mole of PETN. This computed equilibrium mixt matches almost exactly the compn found by Ornellas (Ref 3) for unconfined, or for that matter confined, PETN.

Similar computations for HMX or TNT also match the respective compns found by Ornellas (Refs 4 & 6) for unconfined HMX or TNT. This is to be expected since rapid pressure release in unconfined samples prevents accumulation of appreciable amounts of the products of reactions (3) thru (6).

Theoretical Detonation Product Compositions.

Except for oxygen-balanced expls, the computation of detonation products depends strongly on the choice of the equation of state (EOS) for these products. In the US the BKW EOS (see Vol 4, D272-R) has been favored and most of the computed product compns below will be based on it. Some of these will be compared with the relatively few calcs based on a Lennard-Jones-Devonshire (LJD) EOS (see Vol 4, D287-L).

CJ state product compns calcd via the BKW EOS are compared with compns computed with LJD types of EOS in Tables 2–4. For PETN (Table 2) an early variant of the LJD EOS (Ref 1) shows no solid C in the products and somewhat more CO than the BKW computation. Note that for PETN both EOS give product compn that show relatively little variation with $\rho_0$, the initial density of the expl. This is not the case for RDX and TNT (Tables 3 & 4) where a change in $\rho_0$ results in substantial changes in product compn.

For RDX and TNT a modern form of the LJD EOS (JCZ-3) was used (Ref 5). Note that this EOS gives substantial amounts of $NH_3$ in the products. This is rather startling since the JCZ-3 calcs give lower pressures and higher temps than BKW calcs. Both these effects are in the direction of reducing rather than increasing the amount of $NH_3$ formed, unless
some drastic gas imperfection effects radically change the well-known behavior of reaction (6) (Haber synthesis) at CJ conditions

"Measured" Product Compositions.

Actual measurements of detonation products at CJ conditions do not exist for pure expls, but may be available for expl mixts with inerts. By far the best efforts to measure product compns were made by Ornellas & co-workers (Refs 3, 4 & 6) who made accurate calorimetry and compn measurements on highly confined and unconfined expl samples. The expls he studied were: PETN, HMX, NM, TNT, Bis(2,2-dinitro-2-fluoroethyl)formal (FEFO), 1,2-Bis(difluoroamino)propane (1,2 DP), Benzotrifuroxan (BTF), LX-11-0 (80.1/19.9 HMX/Viton), XTX-8003 (80/20 PETN/Sylgard 182), and three Hydrazine Nitrate (HN) mixts. Of course, most of these measured compns are not CJ products, but reequilibrated mixts of CJ products at some frozen equilibrium temp $T_f < T_{CJ}$.

Ornellas found that for PETN, sample confinement had practically no effect on product compn, which in all cases was very close to that shown earlier in the article in the illustration of an ideal gas equilibrium calcn. We used $T=1600^\circ K$ for our calcn, which apparently corresponds quite closely to $T_f$ for PETN. Measurements on unconfined samples are not reported for NM, FEFO, 1,2 DP and the HN mixts. In all the remaining expls, product compn was strongly affected by confinement. In general, confined samples of these materials produced more $C_{(g)}$ and less CO than unconfined samples

Table 2
PETN—CJ State

<table>
<thead>
<tr>
<th></th>
<th>$\rho_0=1.4\text{g/cc}$</th>
<th>$\rho_0=1.0\text{g/cc}$</th>
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<tr>
<td></td>
<td>BKW (Ref 2)</td>
<td>LJD (Ref 1)</td>
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<tr>
<td>CO₂</td>
<td>3.47</td>
<td>3.29</td>
</tr>
<tr>
<td>CO</td>
<td>1.07</td>
<td>1.67</td>
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<tr>
<td>C₆H₆</td>
<td>0.46</td>
<td>none</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0008</td>
<td>0.033</td>
</tr>
<tr>
<td>H₂O</td>
<td>3.99</td>
<td>3.73</td>
</tr>
<tr>
<td>H₂</td>
<td>0.06</td>
<td>0.20</td>
</tr>
<tr>
<td>N₂</td>
<td>2.00</td>
<td>1.99</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.003</td>
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</table>

*All compns in moles of product/mole expl

Table 3
RDX—CJ State

<table>
<thead>
<tr>
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<th>$\rho_0=1.8\text{g/cc}$</th>
<th>$\rho_0=1.0\text{g/cc}$</th>
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<tbody>
<tr>
<td></td>
<td>BKW (Ref 2)</td>
<td>JCZ-3 (Ref 5)</td>
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<tr>
<td>CO₂</td>
<td>1.49</td>
<td>2.39</td>
</tr>
<tr>
<td>CO</td>
<td>0.022</td>
<td>0.132</td>
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<tr>
<td>C₆H₆</td>
<td>1.49</td>
<td>0.478</td>
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<tr>
<td>CH₄</td>
<td>none**</td>
<td>0.001</td>
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<tr>
<td>H₂O</td>
<td>3.00</td>
<td>1.09</td>
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<tr>
<td>H₂</td>
<td>none**</td>
<td>0.005</td>
</tr>
<tr>
<td>N₂</td>
<td>3.00</td>
<td>2.36</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.00003</td>
<td>1.27</td>
</tr>
</tbody>
</table>

*All compns in moles of product/mole expl
**Less than $10^{-2}$ moles/mole

Table 4
TNT—CJ State

<table>
<thead>
<tr>
<th></th>
<th>$\rho_0=1.6\text{g/cc}$</th>
<th>$\rho_0=1.0\text{g/cc}$</th>
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<tr>
<td></td>
<td>BKW (Ref 2)</td>
<td>JCZ-3 (Ref 5)</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.64</td>
<td>1.97</td>
</tr>
<tr>
<td>CO</td>
<td>0.230</td>
<td>0.474</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>5.13</td>
<td>4.42</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.0003</td>
<td>0.03</td>
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<tr>
<td>H₂O</td>
<td>2.495</td>
<td>1.47</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0013</td>
<td>0.033</td>
</tr>
<tr>
<td>N₂</td>
<td>1.499</td>
<td>1.55</td>
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<tr>
<td>NH₃</td>
<td>0.0015</td>
<td>0.630</td>
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</table>

*All compns in moles of product/mole expl

Table 5
Comparison of Measured TNT Products with Isentropic Compositions

<table>
<thead>
<tr>
<th></th>
<th>Measured for $\rho_0=1.53\text{g/cc}^*$</th>
<th>JCZ-3 Isentropic Compositions for $\rho_0=1.66\text{g/cc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BKW (Ref 2)</td>
<td>JCZ-3 (Ref 5)</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.25</td>
<td>1.24</td>
</tr>
<tr>
<td>CO</td>
<td>1.98</td>
<td>1.97</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>3.65</td>
<td>3.62</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.099</td>
<td>0.17</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.60</td>
<td>1.55</td>
</tr>
<tr>
<td>H₂</td>
<td>0.46</td>
<td>0.47</td>
</tr>
<tr>
<td>N₂</td>
<td>1.32</td>
<td>1.45</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.162</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* Highly confined samples
** Moles product/mole expl
Table 6
Comparison of Measured RDX Products with Isentropic Compositions

<table>
<thead>
<tr>
<th></th>
<th>Measured for $\rho_0=1.89$g/cc</th>
<th>JCZ-3 Isentropic Compositions for $\rho_0=1.89$g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ref 4)</td>
<td>(Ref 5)</td>
</tr>
<tr>
<td></td>
<td>$T=1986^\circ$K $T=1551^\circ$K</td>
<td>$T=2344^\circ$K</td>
</tr>
<tr>
<td>CO</td>
<td>1.44</td>
<td>1.41</td>
</tr>
<tr>
<td>CO</td>
<td>0.80</td>
<td>1.06</td>
</tr>
<tr>
<td>C₃H₅N₃O₆</td>
<td>0.74</td>
<td>0.42</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.03</td>
<td>0.11</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.39</td>
<td>2.12</td>
</tr>
<tr>
<td>H₂</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>N₂</td>
<td>2.76</td>
<td>2.88</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.29</td>
<td>0.24</td>
</tr>
</tbody>
</table>

* Measurements were made for HMX. The values shown are 3/4 of the corresponding product in Ref 4, since RDX is C₃H₅N₃O₆ and HMX is C₄H₆N₆O₆. Highly confined samples

** Moles product/mole expl

For confined expls, Ornellas found that measured comps generally matched comps computed along CJ isentropes if the isentrope temp was between 1500 and 1800°K for BKW-type calcns, and 1800 to 1900°K for LJD calcns of the type used in Ref 1. Agreement between observed and computed values was poor for FEFO. For the three HN mixts, CJ temps are low (all below 1500°K). Quite possible these comps are close to actual CJ comps.

For unconfined samples of PETN, HMX, LX-11-0, TNT, BTF & XTX 8003, calcns assuming ideal gas equilibria also match observed comps if the calcns are made for temps in the range of 1500 to 1800°K.

The modern version of LJD, however, suggests that $T_f$ is greater than 1500–1800°K. As shown in Tables 5 & 6, JCZ-3 isentrope calcns indicate that $T_f=2000^\circ$K for RDX and TNT or slightly greater than the older type LJD isentrope calcns. At present no objective choice appears possible between freeze out temps in the 1500–1800°K range (BKW & ideal gas) or the 1800–2000°K range (LJD)


Progressite. An expl patented by Turpin of Fr in 1882 contg Ba nitrate 65, Amm picate 15, DNB 10, coal tar 6, and brown or red charcoal 4%

Refs: 1) J.P. Cundill, MP 6, 108 (1893) 2) Daniel (1902), 651

Progressites. Permissible expls invented about 1896 by A.G. Dynamit Nobel in Ger. Typical formulations contd: (a) AN 94–95 & aniline hydrochloride 6–5%; (b) AN 89.1–92.2, amm sulfate 6.1–2.3, and aniline hydrochloride 5.5%, with or without 1.2% sulfur added

Refs: 1) Daniel (1902), 652 2) J. Sauer, SS 2, 112 (1907) 3) Anon, SS 8, 398 (1913) 4) Marshall 1, 398 (1917)

Projectiles. See under Ammunition in Vol 1, A383-L to A391-L

The following is a compilation of current (July 1976) unclassified US mil specs on projectiles:

Written by J. ROTH
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<td>30 June 55</td>
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<td>MIL-P-46541</td>
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<td>Smoke WP-t, M357 for 120MM Gun, M58, Assembling, Marking and Packing</td>
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<td>Projectile, Smoke, WP, 57MM, M308A1 Metal Parts Assembly</td>
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<td>05 May 72</td>
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<td>Projectile, Tp-t, 105MM, M468 Metal Parts Assembly</td>
<td>MIL-P-50793 (1)</td>
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<td>MIL-P-60811 (1)</td>
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<td>Projectile, Tp-t, 152MM, XM411E1 Metal Parts Assembly</td>
<td>MIL-P-60815A (3)</td>
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<td>Projectile, Training, 8 Inch, XM440 SHIPPING Assembly</td>
<td>MIL-P-50890</td>
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<td>Projectile, Training, 8 Inch M423, Shipping Assembly</td>
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<td>Projectile, 105MM, Illuminating, XM314A2E1 Metal Parts Assembly</td>
<td>MIL-P-14852A</td>
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<td>Projectile, 105MM, Smoke, Be, M84E1 Metal Parts Assembly</td>
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<td>MIL-P-60547C (1)</td>
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<td>Projectile, 105MM, HE, M1 (HF-1) Metal Parts Assembly</td>
<td>MIL-P-50784</td>
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<td>Projectile, 105MM, Smoke, WP, M60 Metal Parts Assembly</td>
<td>MIL-P-60548A (1)</td>
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<td>Projectile, 105MM, Smoke, WP, M60E1, FILLING Assembly</td>
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<td>Projectile, 152MM, Tp-t, M411A1 Metal Parts Assembly</td>
<td>MIL-P-50369A</td>
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<td>Projectile, 155 Millimeter Howitzer, M121A1, Vx-filled, Without Fuze</td>
<td>MIL-P-60077A</td>
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<td>Projectile, 155-MILLIMETER Howitzer, M121, And Gun, M122, Gb-filled</td>
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<td>Projectile, 155-MM Gun And Howitzer, M104 and M110, WP, Fs, Hd And H Filling Assemblies</td>
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<td>Projectile, 155MM, Smoke, WP, M110 Loading, Assembling and Packing</td>
<td>MIL-P-60477A</td>
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<td>Projectile, 155MM, Velocity Test, T5119</td>
<td>MIL-P-50290 (2)</td>
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<td>Projectile, 155MM, Cs, Tactical, XM631 Assembling and Packing</td>
<td>MIL-P-60419</td>
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<td>Projectile, 155MM, HE, M449A1, Body Assembly For</td>
<td>MIL-P-50535</td>
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<td>Projectile, 155MM, HE, M449A1, Hardware For</td>
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<td>Projectile, 155MM, HE, M692 And M731, Non-metallic Hardware For</td>
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<td>Projectile, 155MM, HE, M483A1 Loading, Assembling And Packing</td>
<td>MIL-P-48749 (2)</td>
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<td>Projectile, 155MM, HE, M107 Loading, Assembling And Packing</td>
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<td>Projectile, 155MM, HE, M470 Loading, Assembling And Packing</td>
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<td>Projectile, 155MM, HE, M483A1 Adapter For</td>
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<td>Projectile, 155MM, HE, M483A1 Metallic Hardware For</td>
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<td>Projectile, 155MM, HE, M692 And M731, Metallic Hardware For</td>
<td>MIL-P-48188</td>
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<td>Projectile, 155MM, HE, Rap, XM549 (With Warhead And Motor Body) Loading, Assembling and Packing</td>
<td>MIL-P-50578B</td>
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<td>Projectile, 155MM, HE, Rocket Assisted M549, Accessories For</td>
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<td>Projectile, 155MM, HE, Rocket Assisted M549, Delay Assembly For</td>
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<td>Projectile, 155MM, HE, Rocket Assisted XM549, Delay Assembly Parts For</td>
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<td>Projectile, 155MM, HE, Rocket Assisted, M549, Inert, Simulated Parts And Loading</td>
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<td>Projectile, 155MM, HE, XM483 Non Metallic Hardware For</td>
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<td>Projectile, 155MM, Illuminating, M485A2, Parts for</td>
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<td>Projectile, 155MM, M483A1 Metal Parts</td>
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<td>Projectile, 155MM, Smoke (Hc and Colored), Be, M116B1 and M116E2, Assembling and Packing</td>
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<td>Projectile, 155MM, Smoke, Be, M116E2, Parts For</td>
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<td>Projectile, 155MM, Smoke, WP, M110 Metal Parts Assembly</td>
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<td>Projectile, 155MM, Test, M692 Loading, Assembling and Packing</td>
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<td>Projectile, 155MM, Training XM455 Shipping Configuration</td>
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<td>Projectile, 155MM, XM687 Metal Parts Assembly</td>
<td>MIL-P-50702</td>
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<td>Projectile, 175 Millimeter, WP, XM510E1, Filling Assembly</td>
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<td>Projectile, 175MM, HE, M437 Metal Parts Assembly</td>
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<td>Projectile, 175MM, HE, M437E2 For 175MM Gun Loading, Assembling, And Packing</td>
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<td>Projectile, 20MM, Api, M53 Metal Parts</td>
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<td>Projectile, 20MM, Dummy, M51A2</td>
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<td>Projectile, 20MM, Hei, M97A2, Metal Parts</td>
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<td>Projectile, 20MM, Heit-sd, XM246 Metal Parts</td>
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<td>Projectile, 20MM, HE1 M56E5, Metal Parts</td>
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<td>Projectile, 20MM, Hei-T, M242, Metal Parts</td>
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<td>Projectile, 20MM, Target Practice, M55A3 And M55A3B1</td>
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<td>Projectile, 20MM, Target Practice, M99A1</td>
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<td>Projectile, 4.2 Inch Tactical Cs, XM633 Metal Parts Assembly</td>
<td>MIL-P-14829 (1)</td>
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<td>Projectile, 4.2 Inch, Tactical Cs, XM633 Loading, Assembling and Packing (For Cartridge, Tactical Cs, XM630)</td>
<td>MIL-P-14901</td>
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<td>Projectile, 4.2 Inch, Illuminating, M335A2 Loading, Assembling and Packing</td>
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<td>Projectile, 4.2 Inch, Illuminating, M335A2 Metal Parts Assembly</td>
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<td>Projectile, 4.2 Inch, Smoke, M328A1, WP Filling</td>
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<td>Projectile, 57 MM, Smoke, WP, M308A1, Filling Assembly</td>
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<td>Projectile, 60MM, Mortar, M302, WP Loading Assembly</td>
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<td>Projectile, 8 Inch, Chemical Agent Gb, M426,</td>
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<td>Projectile, 8 Inch, HE, M404 Loading, Assembling And Packing</td>
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<td>Projectile, 8 Inch, HE, XM509 Adapter For</td>
<td>MIL-P-48094</td>
<td>02 Mar 73</td>
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<td>Projectile, 8 Inch, HE, M106, Loading, Assembling, And Packing</td>
<td>MIL-P-46258B (2)</td>
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<td>Projectile, 8 Inch, HE, M404 Body Assembly And Base Plug For</td>
<td>MIL-P-50526A (2)</td>
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<td>Projectile, 8 Inch, M424A1 Loading Assembly</td>
<td>MIL-P-50562(3)</td>
<td>15 Mar 76</td>
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<td>Projectile, 8 Inch, XM509 Metal Parts Assembly</td>
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<td>Projectile, 8 Inch, Chemical Agent Vx, M426,</td>
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*OS — Commander
Naval Sea Systems Command
Engineering Support Division
Dept of the Navy
Washington, DC 20360

**PA — Commander
Picatinny Arsenal
Dover, NJ 07801

***MU — Commander
Frankford Arsenal
Philadelphia, Pa 19137

****MR — Director
US Army Materials and Mechanics Research Center
Watertown, Mass 02172

*****EA — Commander
Edgewood Arsenal, Md 21010
Prométhée (Fr). See under Explosifs 03 in Vol 6, E363-L

Proof. A ballistic test of weapons or ammo to determine suitability. For propfihs, proof also includes chemical and stability tests. For armor, it includes a test to indicate resistance to bullets. A proof charge is a propellant charge used in the initial firing tests of a gun. For test purposes, it may sometimes exceed normal pressures intended for use in the gun. A proof firing is the firing of certain rounds for the purpose of testing the serviceability of a weapon or its mounts. A proofmark is a distinguishing mark on a weapon to indicate inspection and proof firing. Ref. J. Quick, “Dictionary of Weapons and Military Terms”, McGraw-Hill, NY (1973), 358

Propogation Tests. See under Gap Tests in Vol 6, G1.3-R and Influence Tests in Vol 7, 19B-R to I100-R

Propane and Derivatives

Propene (Dimethylmethane, Propylidine), CH₃CH₂CH₃, mw 44.09; colorless gas; mp =-187.7⁰; bp =-42.1⁰; d of liq at 0⁰, 0.53g/cc, of vap at 0⁰ (air=1) 1.56g/cc; RI at =-42.1⁰, 1.3397. Sol in eth & alc, sl sol in w. Derived from petroleum and natural gas.


Nitropropanes. C₃H₇NO₂, mw 89.09, N 15.72%, OB to CO₂ =-134.7%

1-Nitropropane. CH₃COCH₂NO₂; colorless liq, mp =-108⁰; bp 132⁰; d 1.003g/cc at 20/20⁰; RI 1.4015 at 20⁰, fl pt 34⁰; autoignition temp 789⁰F. Sl sol in w (1.4ml/100ml); 0.5ml w dissolves in 100ml of 1-Nitropropane; misc with many org solvents. Prep by the vapor-phase nitration of propane (Refs 1 & 3)

It is moderately toxic, flammable, and a moderate fire risk. Tolerance, 25ppm in air. It is a moderate expn hazard when shocked or heated (Ref 8)

1-Nitropropane has been evaluated as a solvent and plasticizer for NC (Refs 2, 4 & 6), a recryst agent for RDX (Ref 5), an ingredient of a foamed liq exp for mine-field clearance (Ref 7), and as an intermediate rocket propellant (Ref 9)


2-Nitropropane. CH₃CHNO₂CH₃; colorliq, mp =-93⁰; bp 120.3⁰; d 0.9821g/cc at 25/4⁰; RI 1.3944; fl pt 24⁰; autoign temp 80²F. Sl sol in w (1.7ml/100ml); 0.6ml w dissolves in 100ml of 2-Nitropropane; misc with many org solvents. Prep, toxicity, hazard potential and uses are the same as for 1-Nitropropane

1,1-Dimethyl-1-Nitropropane Dinitrate.

CH₂ONO₂ C₅H₅N₂O₆; mw 239.17; N 17.57%; OB to CO₂

CH₂CH₂CONO₂ =-43.5%; liq. Prep by condensing formaldehyde with CH₂ONO₂ 1-Nitropropane in an alkaline medium and nitrating the product. It is a poor gelatinizer for blasting sol NC

Power. 92% blasting gelatine by BalMort
Stability. 5 minutes in 82.2° Heat Test
Refs: 1) Bell - not found 2) Blatt, OSRD 2014 (1944)

Dinitropropanes. C₃H₆N₂O₄; mw 134.09; N 20.89%; OB to CO₂ =-59.7%

1,1-Dinitropropane. CH₃CH₂CH(NO₂)₂; oily
yel liq (acidic); bp 189°-90°; d 1.258g/cc at 22°. Can be prepd from 1-chloro-1-nitropropane, K hydroxide and K nitrite (Ref 2). V sl sol in w, with an acidic reaction; sol in alcohols.

1,1-Dinitropropane is an expl comparable in its power and sensitivity to TNT. Its thermal stability is satisfactory (does not expld to 360°; at 135°, acid in 30 mins, no expln in 300 mins) (Ref 2).

Qₚ 3349cal/g, H₂O liq, or 3270, H₂O gas (Ref 3). Impact sensy 100cm+ with 2kg wt, BuMines app. One drop of the material was placed on a filter paper disc the same diameter as the striker of the app (Ref 4).


1,3-Dinitropropane. CH₃NO₂CH₂CH₂NO₂; colorless or pale yel oily liq; mp -21.4°; bp 103° at 1mm; d 1.353g/cc at 25.5°; RI 1.4638 at 25°. V sl sol in w, sol in eth.

It was prepd by Keppler and Meyer (Ref 2) by treating 1,3-diliodopropane with Ag nitrate; the product obtained was very unstable. Urbanski and Slon (Ref 3) later prepd it in small quantities, together with 1-nitropropane, on treating n-propane vapor with gaseous nitrogen. More recently, Kispersky et al (Ref 5) prepd a product from 1,3-diliodopropane and Ag nitrate which was stable for at least 9 months.

Its Na compd, C₃H₃(NO₂)₂Na, was prepd by Keppler and Meyer (Ref 2), and was reported to be a violent expl ("heftig explodierendes pulver" in Ger).


2,2-Dinitropropane. CH₂C(NO₂)₂CH₂; white crys with a camphor-like odor; mp 53° with subl; bp 185.5°; d 1.261g/cc; subl at RT. V sl sol in w and insol in alcohols. Was first prepd in 1876 by the oxidation of propylhydroxinitropropane, CH₃C(NO)(NO₂)CH₂, with chromic acid, or by simply heating it in air at 100° (Ref 2).

Nef (Ref 3) prepd it, among other products, by treating Ag dinitroethane with methyl iodide.

2,2-Dinitropropane is an expl comparable with Tetryl in power (12.3% TNT) and with TNT in impact sensitivity. Qₚ 427.8kcal/mole. Initiation temp is 360° in 5 secs. It loses 5.6% by wt in the 75° International Test, and is efflorescent.


1,3-Dinitro-2,2-Dimethylpropane. See under 2,2-Dimethyl-1,3-dinitropropane or Dinitronepropane in Vol 5, D1368-R.

Propanediols and Derivatives

1,2-Propanediol (1,2-Propylene glycol, 1,2-Di-hydroxypropane, Methyl glycol). CH₃CHOH.CH₂OH; mw 76.09; colorless, viscous, stable, hygr liq; bp 187.3°, d 1.0381g/cc at 20/20°; RI 1.4293 at 27°; fl pt (open cup) 210°F; autoignition temp 780°F. Misc with w, ales, and many org solvents in all proportions. Can be prepd by hydration of propylene oxide. On nitration it yields the expl 1,2-Propanediol Dinitrate (see below).


1,2-Propanediol Dinitrate (Methyl Glycol Dinitrate). CH₂CH(NOONO₂)₂; mw 166.09; N 16.87%; OB to CO₂ 28.9%; colorless, oily liq; mp -42.5°; does not freeze at -20°; bp 92° at 10mm; d 1.3774g/cc at 20/4°; RI 1.42720 at 20°; viscosity in poise, 0.0465 (20°); dielectric const 26.80 (20°) (Refs 8 & 9).

1,2-Propanediol Dinitrate was prepd by L. Henry (Ref 2) by slowly pouring propylene oxide into cooled nitric acid, followed by the addition of concd sulfuric acid. Naodm (Ref 5) nitrated 1,2-propylene glycol with 5p of mixed acid contg 40% nitric and 60% sulfuric acids at 20° to give, in 86% yield, a product with a nitrogen content of 16.5%. A mixed acid contg 47.5% nitric, 45.5% sulfuric and 7% w was used by Matignon et al (Ref 6) at 10°. By using a
10% excess of nitric acid, they achieved a yield of 91–93%.

It is insol in w; sol in alc, eth or strong nitric acid; gelatinizes NC.

As early as 1904, 1,2-Propanediol Dinitrate was proposed (Ref 3) as an additive to lower the freezing temp of NG, but its practical application on a large scale was hindered by lack of the raw material, propene-1,2-diol. It is only recently that the synthesis of glycol from ethylene led to the development of a method for producing methyl glycol from propylene via cyanohydrin. Even so, propylene-1,2-glycol is somewhat more expensive than glycols derived from ethylene (Ref 9).

1,2-Propanediol Dinitrate is a HE, the properties of which were detailed by Barab (Ref 4), Naoûm (Ref 5) and the Hercules Powder Co (Ref 8):

**Heat of Formation.** 83.1 kcal/mole

**Heat of Explosion.** 1109 kcal/kg at const vol with H₂O gaseous

**Power.** 540 ml or 92% NG by Trauzl Pb block test with w tamping

**Sensitivity to Impact.** Less sensitive than NG

**Stability.** 60 minutes in 71° KI test

**Velocity of Detonation.** 6885 m/sec and 2000 m/sec (?), as detd in 10 mm ID glass tubes with 1 mm wall (Ref 8)

**Vapor Density.** 3.8% loss in wt at 35° of a 10g sample in a 60 mm diam dish after 24 hrs; after 3 days, 4.1%.

**Note:** A mixt consisting chiefly of 1,2-Propanediol Dinitrate, but contg varying amts of ethylene glycol dinitrate and butylene glycol dinitrate was marketed under the tradename Nitroxyronel (Ref 8)


1,3-Propanediol (Trimethylene glycol, 1,3-Di-hydroxypropane). CH₂OH.CH₂.CH₂OH; mw 76.09; colorl to pale yel, very visc, sweet liq; mp, freezes in a mixt of dry ice and eth; bp 210–120; d 1.0597 g/cc at 20/4°; RI 1.4398 at 20°. Misc with w, alc; insol in eth, benz or clful. Can be prepd by reduction of ethyl glycidate with LiAI hydride. On nitratin it yields the expl 1,3-Propanediol dinitrate (see below)

**Refs:** 1) Beil 1, 475 & (247) 2) Naoûm, NG (1928), 229 3) Merck (1976), 1246-R (No 9384)

1,3-Propanediol Dinitrate (Trimethylene glycol Dinitrate). O₂NOCH₂.CH₂.CH₂ONO₂; mw 166.09; N 16.87%; OB to CO₂ −28.9%; nearly colorl; oily liq with a slight aromatic odor; mp −38°; bp 108° at 10mm, decomp at about 185° with evolution of yel fumes and deflagramates at 225°; d 1.4053 at 16/16°, 1.3952 at 20/4°; RI 1.43476 at 20°; viscosity in poise, 0.0940 (6.3°), 0.0550 (20.2°), 0.0275 (54.2°); dielectric const 18.97 at 20°; dipole moment 3.50 (Ref 6)

Nearly insol in w, easily sol in alc, eth, etc, benz; gelatinizes NC. Can be prepd by the nitration of 1,3-propanediol mixed with nitric-sulfuric acid, as described by Naoûm (Ref 4) and Blechta (Ref 3). The nitration requires a lower temp than that used for nitrating glycerin, because the central methylene group is readily oxidized at a higher temp. A temp between 0–10° is recommended since decomp is possible even at 15°, while at 20° yel fumes are evolved. Separating the product from the spent acid occurs with ease at 10°. From 100p of 1,3-propanediol, 198p of the dinitrate are produced corresponding to 90.6% of theoretical.

1,3-Propanediol Dinitrate is a powerful and brisant expl which is less sensitive than NG, and has satisfactory stability. Following are some of its properties, as given in Refs 2, 3, 4, 5 & 6, and by the Hercules Powder Co:

**Heat of Explosion.** 1138.5 kcal/kg (w as vapor)

**Heat of Formation.** 78.1 kcal/mole

**Power.** 540 ml or 92% NG by Trauzl Pb block test with w tamping

**Sensitivity to Impact.** Very low; a 2kg wt falling 100cm fails to initiate an expln

**Stability.** 45 minutes in 83° KI test. Storage at 75° for 25 days caused no decomp or development of acidity

**Toxicity.** Similar to that of NG
Immm wall

Volutility. 1.8% loss in wt at 35\(^\circ\) of a 10g
sample in a 60mm diam dish after 24 hrs; after
3 days, 4.2%.

Notes: It was proposed for use as an antifreeze
addition to Dynamites. A blasting gelatine
consisting of 93% 1,3-Propanediol Dinitrate
and 7% colloidion cotton gave a Pb block ex-
pansion of 470mL, or about 80% of the effect
produced by the same gelatine contg NG

1,3-Propanediol Dinitrate was present in NG
prepd in Ger by nitrating synthetic glycerin,
called Protol

Refs: 1) Beil - not found 2) J. Barab, USP
1371215 (1921) 3) F. Blechta, SS 17, 57–8
(1922) 4) Naoum, NG (1928), 231–36
5) Davis (1943), 233–34 6) Urbański 2,
3, 4 & 155–57 (1965)

Propanediol Dinitrate (Commercial). Barab
(Ref 4) patented liq exps contg varying amts
of 1,2- and 1,3-Propanediol Dinitrates. These
mixts were claimed to be as powerful as, but
less sensitive than NG. The product was ex-
amined by the US BuMines and found to make
up a 40% straight Dynamite that compared
favorably with 40% straight NG Dynamite

Ref: J. Barab, USP 1371215 (1921)

2-(3',5'-Dinitrophenyl)-2-Nitro-1,3-Propanediol
Dinitrate. \(C_9H_6N_2O_8\); mw 377; N 18.6%; OB
to CO\(_2\) –66.5%; mp 114–115\(^\circ\); d 1.70g/cc;

\[
\begin{array}{cccc}
O_2N & CH_2ONO_2 & CHNO_2 & O_2N \\
\end{array}
\]

Qc 1022.9cal/mole. Prepd by condensing
phenylnitromethane with formaldehyde, and
nitrating the product

Sensitivity. Slightly less sensitive than PETN
Power. 126% TNT by BalMort
Stability. Ignites at 360\(^\circ\); thermal stability at
135\(^\circ\); acid in 60 mins, no expln in 300 mins

Hygroscopicity. Gains 0.05% at 100% RH

Ref: 1) Beil – not found 2) Blatt, OSRD
2014 (1944)

1-Propanol (n-Propyl alcohol, Propylic alcohol,
Optal). \(CH_3CH_2CH_2OH\); mw 60.09; liq; mp
-127\(^\circ\); bp 97.2\(^\circ\); d 0.8053g/cc at 20/4\(^\circ\); misc
with w, alc & eth. Available as a by-product of
the reaction between CO and H\(_2\).

Ref: Merck (1976), 1016-L (No 7630)

Dinitropropanols. \(C_3H_6(NO_2)_2OH\); mw 150.10;
N 18.7%; OB to CO\(_2\) –42.7%

2,2-Dinitro-1-Propanol. \(CH_3C(NO_2)_2CH_2OH\);
cryts; mp 88\(^\circ\). Can be prepd by the action of
formaldehyde on 1,1-dinitroethane. It is an expl
comparable in power to Tetryl and in sensi-
tivity to TNT. It is slightly hygroscopic and
fairly stable

Note: A eutetic mixt of the formal and acetal of
2,2-Dinitropropanol (DNPAF) is used as the
plasticizer in a plastic-bonded expl (PBX-9501)
contg 95 wt % HMX, 2.5% Estane as the plastic
bonding agent, and 2.5% DNPAF. It is claimed
to have an expl energy comparable to that of
PBX-9404 [94% HMX, 3% NC & 3% tris-(β-
chloroethyl) phosphate (CEF)], but possesses
greater temp stability and significantly better
handling safety [T.M. Benziger, USP 3778319
(1973)]

1,1-Dinitropropanol (Dinitroisopropyl alcohol).
\((O_2N)_2CH.CHOH.CH_3\); colorl oil; bp, de-
flaigrates on heating above 120\(^\circ\); d 1.33g/cc at
15/4\(^\circ\); RI 1.449 at 15\(^\circ\); sol in w (1 p in 5–6p).
Can be prepd by treating its K salt with dil
sulfuric acid. The K salt is prepd from K di-
nitromethane and acetaldehyde

Refs: 1) Beil 1, 366 2) Blatt, OSRD 2014
(1944)

1,3-Diazidoisopropyl Alcohol (1,3-Diazido-
propanol-2). \(N_3CH_2.CHOH.CH_2N_3\); mw
142.13; N 59.14%; colorl, odorless liq; bp
88–91\(^\circ\) at 0.6mm; d 1.2687g/cc at 21/4\(^\circ\). Can
be prepd by reacting 1,3-dichlorohydrin with Na
azide on a steam bath for 12 days in the dark.
It expls on impact, when ignited, or when in
contact with concd sulfuric acid. Several expls
were reported when attempting to det its nitro-
gen content by combustion

Refs: 1) Beil 1, (186) 2) J.C. Philip, JCS
101, 493–96 & 1866–71 (1912)

1,3-Dinitramino-2-Propanol Nitrate. \(C_3H_7N_5O_7\);
CH₂NHNO₂
| CHONO₂
| CH₂NHNO₂

Preparation

H₂NCH₂CHOHCH₂NH₂ → CH₂NH₂CO₂C₂H₅
| CH₂OH
| CH₂NH₂CO₂C₂H₅

CH₂N(NO₂)CO₂C₂H₅
| CH₂N(NO₂)CO₂C₂H₅
| CH₂NH₂CO₂C₂H₅

Hygrosopicity. Gains 0.02% at 100% RH

Power. 142% TNT by BalMort

Sensitivity. Impact, with Bruceton No 3 machine, 50% positive with 5kg wt at 24cm

Stability. Deflagrates at 230°; thermal—no acid in 300 mins at 100°; acid in 105 mins at 135°; vacuum—1.99 to 4.36cc in 48 hrs at 100°

Refs: 1) Bell — not found  2) Blatt, OSRD 2014 (1944)


Propanolamines. See under Aminopropanols and Derivatives in Vol 1, A253-L

Propanolamines. See under Anilinopropanol and Derivatives in Vol 1, A436-L

Propargyl Alcohol (2-Propyn-1-ol). HC≡CCH₂OH; mw 56.06; colorless liq; mp −48 to −52°; bp 114−115°; d 0.97g/cc at 20°; RI 1.43064 at 20°; Flash pt 36.1°. Sol in w, alcohols, esters, immisc with aliphatic hydrocarbons. Can be prepd from ethylchlorohydrin and Na or from acetylene and formaldehyde (Refs 5 & 6)

If propargyl alcohol and similar acetylenic comds are dried with alkali before distn, the residue may expl (probably due to salt formation). Na sulphate is recommended as a suitable desiccant (Ref 2)

The addition of P₂O₅ to propargyl alcohol caused the alcohol to burst into flame (Ref 4)

Following the published procedure, hydroxyacetone was being prepd on half the scale by treating propargyl alcohol as a 30% wt aq soln with H₂SO₄ and sulfuric acid (6g + 0.6g per mole of alc, respectively). On stirring and warming the mixt to 70°, a violent exothermic eruption occurred. Quartering the scale of operations to 1 g mole, and reducing the amt of acid to 0.37g/mole, gave a controllable reaction at 70° (Ref 3)


Propargyl Bromide (3-Bromo-1-propyne). HC≡CBr; mw 118.97; color to faintly brownish liq; mp 24.4°; bp 88–90°; d 1.52 g/cc; RI 1.4320 at 20°. Sol in alc, eth, benz & chlfr. Flammable; flash pt 10° (closed), 18° (open); ignition temp 328°; lower flammable limit 3.0%. It can be decomd by mild shock. When heated under confinement, it decomps with exph violence and may detonate. When suitably diluted, as with 20–30% by wt of toluene, its expl properties are practically eliminated (Ref 4)

Pure propargyl bromide will decom p violently or detonate at temps as low as 220° (Ref 2). Liq propargyl bromide is easily ignited by impact from such possible sources as "water hammer" or accidental pressurization of the accelerated liq (Ref 3). Tests at the BuMines showed a mixt of chloropirin and propargyl bromide to be shock sensitive (Ref 3)

PROPPELLANTS, SOLID

I. Introduction

Solid Propellants (SP) are solid substances that can be transformed into gases (usually hot) which act as driving jets in propulsion systems. Propulsion systems can be classified into guns, jet engines and rockets. In a gun the SP propels a "slug" out of the gun barrel. In both jet engines and rockets the SP provides forward thrust by the rearward ejection of fluid jets thru nozzles mounted on the jet engine or rocket. In a rocket the propulsive system (e.g. the SP) requires no contribution from the surrounding medium to produce the exhaust jet, whereas jet engines function by ingesting the surrounding medium (air or water). Thus rockets can function in vacuum (space) but jet engines cannot. It is usually understood that a rocket motor is that part of the propulsion system in which the propellants are transformed into the exhaust jet, while a rocket engine is the entire system — rocket motor, containers, pumps, etc. For solid proplnt rockets, rocket motor and rocket engine are the same piece of apparatus, which is not the case in liq proplnt rockets (see Vol 7, L34-R).

During the past thirty years a tremendous volume of literature has dealt with all aspects of solid propellants. A comprehensive review of all this literature is quite beyond the scope of this Encyclopedia. Indeed an all-inclusive discussion of SP would require an entire Encyclopedia wholly devoted to solid propellants. The impracticality of a comprehensive review is not the only reason for limiting the scope of the present article. Solid propellant literature suffers more than usually from repetition and poor quality. Thus even in a comprehensive review, considerable selectivity of subject material is imperative. Furthermore, as shown below, certain aspects of SP, in particular cannon proplnts, have already been treated in previous Encyclopedia volumes.

Since this Encyclopedia deals primarily with explosives and explosive phenomena, the present article emphasizes the explosion hazards of SP. It also features modern concepts of propellant ignition and combustion. Other aspects of SP such as uses, production methods, physical characteristics, etc., will be treated in less detail, but recent efforts on improving performance will be emphasized. Because previous Encyclopedia articles on SP have emphasized cannon propellants and established practices, the present article, to avoid repetition, will emphasize rocket propellants and modern concepts.

As stated above, various aspects of SP have been presented in previous Encyclopedia volumes. In alphabetical order, they are:

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<td>6, G98–108</td>
<td>1972</td>
</tr>
<tr>
<td>Hygroscopicity of Propellants</td>
<td>7, H252–253</td>
<td>1955</td>
</tr>
<tr>
<td>Hypergolic Propellants</td>
<td>7, H254–259</td>
<td>1973</td>
</tr>
<tr>
<td>Ignition *</td>
<td>7, J11–16</td>
<td>1961</td>
</tr>
<tr>
<td>JATO</td>
<td>7, J67</td>
<td>1959</td>
</tr>
<tr>
<td>Moisture Determination in Propellants (under &quot;Ethanol&quot;)</td>
<td>6, E171–76</td>
<td>1963</td>
</tr>
</tbody>
</table>

* To be updated and revised in the present article
Recent general references on SP in book or pamphlet form are:
B. Siegel & L. Schieler, "Energetics of Propellant Chemistry", Wiley, NY (1964)
A.M. Ball, "Solid Propellants", EngrDesHndbk, AMCP 706-175 (1964)
Anon, "Ballistics Series, Interior Ballistics of Guns", EngrDesHndbk, AMCP 706-150 (1965)

The present article will consist of: a brief History of SP (Section II); Representative SP and Their Uses (Section III); Production Methods of Representative Propellants (Section IV); Physical Characteristics of Representative Propellants (Section V); Chemical Characteristics & Performance (including modern concepts of ignition and combustion) (Section VI); Explosion Hazards (Section VII); and Brief Summaries of Recent Literature on SP (Section VIII)

II. History of Solid Propellants
The earliest solid propellant was Black Powder, also known as Gun Powder. Its history is de-scribed in detail in Vol 2, B165-68 & Vol 7, H117-34. Black Powder is no longer used as a propllnt, but it is still used in igniters for SP

The next stage in the development of SP, namely the early development of single base smokeless powder, followed the discovery of Nitrocellulose (NC). We quote Urbafiski (Ref 46a, p 528):

"A few years after the discovery that the treating of cellulose with nitric acid converts it into a combustible substance, the idea arose of using nitrocellulose as a propellant instead of blackpowder. Schönbein's experiments (Ref 1), repeated by Pelouze (Ref 2), showed the high energy of nitrocellulose. It was found that a charge of nitrocellulose endows a projectile with a penetrating effect similar to that of a triple charge of blackpowder

The primary difficulty in exploiting this property lay in finding a method of manufacturing nitrocellulose. It was not until large-scale manufacture of nitrocellulose was achieved by Lenk (Ref 13) that propellant charges could be used for Austrian artillery. Shortly afterwards, however, this method proved to be unsatisfactory, due to the variable results obtained and to the excessive pressure developed when firing nitrocellulose charges, which in many instances damaged or even blew up the cannon

Earlier observations that nitrocellulose burns very quickly in a confined space - much more quickly than blackpowder - were confirmed. Since it is difficult to reduce the burning rate by physical methods only e.g. by compressing the nitrocellulose to increase its density, attempts were made to slow down the rate of burning by the addition of phlegmatizing substances, such as gums, waxes, fats etc

Partly successful results were obtained by Schultze (Ref 3) who prepared his powder by the following method. Wood cut into 1-2mm grains was purified by boiling in sodium hydr-oxide solution and bleaching with calcium hypo-chlorite. It was then nitrated with a mixture of nitric and sulphuric acids. The nitration product was stabilized by boiling in a sodium carbonate solution, then dried and impregnated with a solution of either potassium or barium nitrate. After drying the grains were polished in a drum with paraffin wax to form a powder of the following composition:
50% nitrocellulose & nitrated hemicelluloses
13% non-nitrated wood pulp
33% potassium and barium nitrates
4% paraffin

This powder, however, was still too fast-burning for use in military rifles, but was found suitable for use in shot guns, and was a forerunner of propellants of the 'Schultzé type' used in some countries (chiefly Great Britain) as sporting powders.

A few years later it was discovered that nitrocellulose dissolves in organic solvents, such as acetone, ethyl acetate and in mixtures of alcohol with ether, leaving on evaporation of the solvent a highly dense, transparent film, which burns more slowly than nitrocellulose itself (Ref 5).

Some investigators tried to make use of this property. Volkmann (Ref 4) improved Schultzé's powder by dipping nitrated grains of wood into a mixture of ether and alcohol and then either mixing them with blackpowder to prevent caking and coating them with a layer of this explosive or compressing the sticky grains into larger cubes. In spite of the encouraging results obtained in using this powder (the size of charges required was half of that of blackpowder) the Austrian authorities stopped manufacture on the formal grounds that the plant concerned infringed their blackpowder monopoly.

A number of patents were then registered for various methods of using solvents to prepare granular powder from nitrocellulose (Spill (Ref 6), Reid (Ref 7), Wolf and Förster (Ref 8)). None of those methods, however, found practical application, except for a short time in the work of Duttenhofer at Rottweil (Ref 14). Duttenhofer nitrated slightly carbonized cellulose, stabilized it and saturated the nitrocellulose so obtained with ethyl acetate until a gelatinized mass was formed. After being dried, the horn-like mass was broken up in a corn mill and the grains so obtained were graded. Clearly, Duttenhofer employed virtually the same production method as that used to manufacture blackpowder.

Duttenhofer's powder was used for a certain time in Germany under the name of RCP (Rottweil Cellulose Pulver). Its greatest disadvantage was the irregularity of the shape of the grains which prevented it from burning as uniformly as the smokeless powder (Ref 11) invented by Vieille at about the same time.

Vieille developed his powder as the result of systematic investigations. In 1879 he began a study of the burning of explosives in a manometric bomb which he invented together with Sarrau.

In the course of studying the burning of blackpowder Vieille found that it can burn in parallel layers provided that its specific gravity is approximately 1.80 or more. He extended his experiments (1882—1884) to nitrocellulose, and tested its behaviour at various densities. Since it turned out that high specific gravity nitrocellulose cannot be achieved simply by pressing, Vieille made use of the recognized method of increasing its specific gravity by treatment with various solvents. He formed the dough-like mass into flakes and thin sheets which on drying showed a fairly high specific gravity (about 1.65). By experiments in the manometric bomb, Vieille demonstrated that the flakes of the new powder burn in parallel layers and that this property makes their time of burning dependent upon their smallest dimension i.e. upon their thickness. Hence by altering this the total time of burning of the flakes may be controlled, and the 'coefficient of the vivacity' (coefficient de vivacité) of the powder

\[
\left[ \frac{dp}{dt} \right]_{\text{max}}
\]

where \( p \) is pressure produced by burning the powder, \( r \) is time of burning, may be determined in the manometric bomb. Thus powders of an adequate vivacity adjusted to a given calibre of arms may be easily standardized.

Shortly afterwards (1885) Vieille's powder was introduced in France under the name of B powder (Poudre B). Vieille utilized two types of nitrocellulose for its manufacture: collodion cotton \( CP_2 \), soluble in a mixture of ether and alcohol and forming the powder dough; cotton \( CP_1 \), insoluble in a mixture of ether and alcohol, incorporated into the powder mass in the form of unchanged fibres.

In Russia, Mendeleyev (Ref 12) worked out a method for the manufacture of smokeless powder from pyrocellulose, i.e. relatively high-nitrated (12.5% N) nitrocellulose soluble in a mixture of ether and alcohol. In 1892 the manu-
ufacture of this powder was started for naval guns. Nitrocellulose powder of this type was soon adopted for military purposes in the USA, where nitrocellulose powder became known as ‘single base powder’.

Double base smokeless powder was first produced by Alfred Nobel. Again we quote Urbanski (Ref 46a, p 530):

..."A second type of smokeless powder, Ballistite, was invented by Alfred Nobel (Ref 9) in 1888. He took advantage of the ability of nitroglycerine to dissolve nitrocellulose and thus replaced a volatile, non-explosive solvent (ether and alcohol in former powders) by a non-volatile explosive solvent – nitroglycerine. The ratio of nitrocellulose to nitroglycerine was 45:55. This is a relatively small amount of nitroglycerine which dissolves nitrocellulose with difficulty. Abel and Dewar (Ref 10) however succeeded in adapting acetone for the manufacture of nitroglycerine powder. This is a solvent of both the active ingredients: nitrocellulose and nitroglycerine. The product – British Cordite – has not been used outside the British Commonwealth. The powders made of nitrocellulose, nitroglycerine and a mixture of ether and alcohol as a solvent achieved only temporary success. The use of any solvent was troublesome and proved a drawback in manufacture, so that nitroglycerine powder without a volatile solvent, derived from ballistite, aroused much greater interest.

Work on the improvement of nitroglycerine powder without a volatile solvent was aimed at the reduction of its content of nitroglycerine. By the selection of a suitable nitrocellulose and by the addition of non-volatile solvents (‘gelatinizing agents’), of the so-called ‘centralite’ type (‘carbamite’ according to English nomenclature) as in Claessen’s (Ref 15) patents, a new type of nitrocellulose powder, the so-called RP-12 or RPC-12, was manufactured from 1912 onwards. This powder was used extensively during World War I since it could be produced much more quickly than nitrocellulose powder. The manufacture of this powder contributed largely to the long resistance of the Central Powers in World War I.

The enormous consumption of smokeless powder during this war led to difficulties in producing a sufficient quantity of nitroglycerine. In Russia and Germany attempts were made to replace part of the nitroglycerine by aromatic nitro compounds such as DNT or ‘liquid TNT’ (an oily mixture of DNT and TNT with isomers of TNT). This powder had several advantages. In comparison with nitroglycerine nitro compounds give a powder with a lower temperature of explosion that produces less erosion and flash. Powders containing nitro compounds with nitroglycerine were later adopted in the USSR.

Attempts to replace nitroglycerine partly or wholly by nitroglycerol had little success due to the high vapour pressure of the latter which facilitates volatilization and, consequently, reduces its ballistic stability (ballistic properties change as nitroglycerol volatilizes). Later, diethyleneglycol dinitrate was tried (nitrodiiglycol, DGDN) and was shown to have great advantages over nitroglycerine. With nitroglycerine, good gelatinization of the nitrocellulose may be obtained if the ratio of nitroglycerine to nitrocellulose is not less than 60:40, whereas with nitrodiiglycol this ratio may be much lower, viz. 20–45 nitrodiiglycol to 80–55 nitrocellulose, since nitrodiiglycol is a better solvent of nitrocellulose than nitroglycerine. This facilitates manufacture and, at the same time produces a more uniformly gelatinized mass. Various alterations may also be introduced in the composition of powder such as an increase in the content of nitrocellulose or on addition of insoluble ingredients, serving, for instance, to suppress flash.

Solventless powder without nitroglycerine (G powder) has a lower heat of explosion, and consequently causes less wear on the bore.

Gallwitz (Ref 16) reports the following data on the influence of the heat of explosion upon the bore wear. With a nitroglycerine powder containing no solvent and giving a heat of explosion of 950 kcal, the barrel stands up to 1700 rounds while with a similar powder giving a heat of explosion of 820 kcal, it withstands 3500 rounds. The reduction of the calorific value of the powder by 130 kcal therefore doubles the useful life of the barrel.

Further reduction of the calorific value of nitroglycerine powder proved to be impossible. But by using nitrodiiglycol instead of nitroglycerine, a powder was obtained with a heat of explosion of 690 kcal, which prolonged the life of the barrel considerably, i.e. to 15,000–17,000...
rounds

A further development led to the invention of flashless powder. Tests carried out in various countries, included the addition of aromatic nitro compounds to nitrocellulose powders and of potassium salts to nitroglycerine powders. Nitroglycerol powder with an addition of 2% K₂SO₄ produced a small flash. During World War II in Germany and Great Britain it was the custom to add a considerable amount of nitroguanidine to nitroglycerol powders. In Germany this was called "gudol" powder (German Gudol Pulver).

Other attempts to improve nitroglycerol powders were based on the introduction of substances such as pentrite (German Nipolith Pulver) and cyclonite. In both cases a powder with a high caloric value was obtained. The manufacture of these powders never went beyond the pilot plant scale."

Triple base propllnts contain NC, NGu and a nitrate ester such as NG or DEGDN. They are laimed to produce less flash & gun barrel erosion than double base propllnts. The earliest triple base proplnt appears to be Guidopulver, developed in Germany in 1937 (see Vol 5, D1537-R), which had NC, DEGDN & NGu as its major ingredients. During WWII many triple base formulations based on NG, NC & NGu were developed and used by the US and its allies (see Vol 5, D1536 & Vol 2, C34–37).

Smokeless powders (single, double & triple base) although excellent as gun propllnts have some disadvantages. It is difficult and costly to produce large size smokeless propllnt grains needed in rockets. The presence of NG creates manufg & use hazards. Moreover, these propllnts can have rather poor stability and consequently require continuous stability checks. Because of these disadvantages, a different type of propllnt, primarily for rockets, began to be developed during WWII. These so-called composite propellants consist of a solid oxidizer dispersed in a solid fuel matrix. They may contain addnl solid fuel such as Al and/or hydrides and additional high energy ingredients such as HMX. Usually the matrix is an elastomer-type material, either polymerizable, castable, or vulcanizable. These propllnts are relatively cheap, stable, and need not contain components that are hazardous per se (eg, no NG). One of the earliest composite propllnts appears to be based on perchlorate salts dispersed in an asphalt matrix (see Vol 3, C464-R).

Recent trends in rocket propllnt development, and most of the recent developments in SP are for rocket and not gun propllnts, were directed toward the attainment of higher energy systems (actually higher specific impulse). Unfortunately, the use of exotic components presents grave stability problems which are yet to be overcome. Some energetic plasticizers have been developed and in some applications specific impulse has been increased substantially by substituting Be for Al. Much of this subject remains classified.

For further historical information the reader is referred to Vol 7, H117–61, which has historica data on propllnts interspersed within information relevant and irrelevant to the history of exps & firearms.

III. Representative Solid Propellants Types and Their Uses

A. Smokeless

By far the largest use of smokeless solid propllnts is in gun propllnts where they are categorized as single-, double-, and triple-base. Typical single-base propllnt formulations use NC as the principal binder and are plasticized with such compds as DNT, dibutyphthalate, and relatively small ams of DEGDN and TEGDN. Stabilizers such as 2-nitrodiphenylamine or ethyl centraile are added to retard the decompn of the NC nitrate group. These propllnts are normally extruded into small cylindrical shapes or ribbons which are chipped. Typical formulations are given in Table 1 (Ref 32a).

As stated, the major uses for these propllnts are for small arms ammo, mortar shells and artillery shells up to 280mm. They are also used as the propelling charge in naval guns.

Double-base compns are primarily NC which is plasticized with NG. Additives are required to reduce sensitivity to expln, flash, and smoke production. Some typical compns are listed in Table 2 (Ref 27, 32a).

At this time the major uses of double-base smokeless compns are in Navy rocket weaponry and gun propllnts. The 2.75-inch FFAR, Sidewinder, SHRIKE, ASROC and Polaris weapon systems employ such propllnts. The major dis-
Table 1
Typical Single-Base Solid Propellants

<table>
<thead>
<tr>
<th>Designation</th>
<th>M6</th>
<th>M10</th>
<th>IMR</th>
<th>EC-NACO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (13.15% N)</td>
<td>87</td>
<td>98</td>
<td>100</td>
<td>91.4</td>
</tr>
<tr>
<td>Ethyl centralite</td>
<td></td>
<td></td>
<td></td>
<td>3.8</td>
</tr>
<tr>
<td>Basic lead carbonate</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Total volatile (ethyl alcohol + dibutyl ether)</td>
<td></td>
<td></td>
<td></td>
<td>3.8</td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td></td>
<td>1</td>
<td>1 (added)</td>
<td></td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>1 (added)</td>
<td>1</td>
<td>0.7 (added)</td>
<td></td>
</tr>
<tr>
<td>Dinitrotoluene</td>
<td>10</td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>3</td>
<td></td>
<td></td>
<td>(deterrent coating)</td>
</tr>
</tbody>
</table>

Table 2
Common Double-Base Solid Propellants

<table>
<thead>
<tr>
<th>Designation</th>
<th>M2</th>
<th>M5</th>
<th>M8</th>
<th>M21</th>
<th>N5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (13.25% N)</td>
<td>77.45</td>
<td>81.95</td>
<td>52.15</td>
<td>53.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>19.50</td>
<td>15.00</td>
<td>43.00</td>
<td>31.00</td>
<td>34.90</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>2.15</td>
<td>2.15</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl centralite</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triacetin</td>
<td></td>
<td></td>
<td></td>
<td>11.00</td>
<td></td>
</tr>
<tr>
<td>Lead salicylate</td>
<td></td>
<td></td>
<td></td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>Lead stearate</td>
<td></td>
<td></td>
<td></td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Diethyl phthalate</td>
<td></td>
<td></td>
<td></td>
<td>3.00</td>
<td>10.50</td>
</tr>
<tr>
<td>2-Nitrodiphenylamine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.00</td>
</tr>
<tr>
<td>Lead salts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.40</td>
</tr>
<tr>
<td>Candelilla wax</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 3
Triple-Base Propellants

<table>
<thead>
<tr>
<th>Designation</th>
<th>M15</th>
<th>M16</th>
<th>M17</th>
<th>M31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroguanidine</td>
<td>54.70</td>
<td></td>
<td>54.70</td>
<td></td>
</tr>
<tr>
<td>Nitrocellulose (13.15% N) (12.6% N)</td>
<td>20.00</td>
<td>55.50</td>
<td>22.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Nitroglycerin</td>
<td>19.00</td>
<td>27.50</td>
<td>21.50</td>
<td>19.00</td>
</tr>
<tr>
<td>Ethyl Centralite</td>
<td>6.00</td>
<td>4.00</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>Sodium aluminum fluoride</td>
<td>0.30</td>
<td></td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td></td>
<td></td>
<td></td>
<td>4.50</td>
</tr>
<tr>
<td>2-Nitrodiphenylamine</td>
<td></td>
<td></td>
<td></td>
<td>1.50</td>
</tr>
<tr>
<td>Dinitrotoluene</td>
<td></td>
<td>10.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium sulfate</td>
<td></td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td></td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead stearate</td>
<td></td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
advantage is the increased sensitivity of these compns to detonation.

Triple-base proplns use primarily NGu as a third major ingredient in addition to NC and NG. Typical compns are shown in Table 3. The major use of this type of propln in is in gun proplns for mortar and artillery shells.

The proplns described above are in the realm of prior art and depict those NC proplns with low smoke potential that are used primarily as gun proplns. Recent research and development work has been concentrated on creating both gun proplns and rocket proplns with reduced smoke output in order to foil countermeasures. Lavitt (Ref 76) found that the concurrent use of optimum proportions of lead stearate and sodium barbiturate in double-base proplns resulted in a marked reduction in smoke output. This was attributed to the synergistic interaction of the two salts to produce more complete oxidation of the exhaust products.

The importance of using the optimum ratio of the two catalysts is demonstrated by the higher smoke values shown in Table 4 for Propellants 105, 106 and 107, when compared to other standard NC base proplns and a standard ammonium nitrate composite propln with about the same flame temp. The attenuation of a beam of light across the exhaust gases was measured for each formulation. Note that these formulations have less energy as measured by the heat of explosion (600–700 cal/gm range) when compared to the standard proplns described previously where $H_{ex}$ is in the 800–900 cal/gm range.

The most common high energy smokeless compns used in rockets employ HMX or RDX in double-base compns to improve the combustion efficiency. However, other rocket proplns employing ammonium perchlorate and high-energy NF compds have yielded low smoke proplns. One such compd, 1,2,3-tris[1,2-bis(difluoramo)-ethoxy] propane (TVOPA) has been investigated as a plasticizer in acrylate-acrylic acid co-polymer binder proplns for this use. However, its high cost led to a search for replacements. Sayles (Ref 77) described the use of butanetriol trinitrate (BTTN) as a partial or complete replacement for TVOPA in high-energy smokeless proplns. The effect of this substitution on the

<table>
<thead>
<tr>
<th>Designation</th>
<th>101</th>
<th>102</th>
<th>103</th>
<th>104</th>
<th>105</th>
<th>106</th>
<th>107</th>
<th>MDB-7</th>
<th>LFT-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition, % (nominal)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrocellulose (12.6% N)</td>
<td>48.3</td>
<td>53.3</td>
<td>48.3</td>
<td>48.3</td>
<td>48.6</td>
<td>48.2</td>
<td>48.1</td>
<td>48.6</td>
<td>–</td>
</tr>
<tr>
<td>Nitroglycerin</td>
<td>27.0</td>
<td>24.2</td>
<td>27.0</td>
<td>27.0</td>
<td>27.0</td>
<td>26.0</td>
<td>27.0</td>
<td>27.0</td>
<td>–</td>
</tr>
<tr>
<td>Triacetin</td>
<td>19.5</td>
<td>14.2</td>
<td>12.5</td>
<td>7.5</td>
<td>19.9</td>
<td>14.5</td>
<td>20.4</td>
<td>18.8</td>
<td>–</td>
</tr>
<tr>
<td>Ethyl Centrate</td>
<td>1.0</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>3.0</td>
<td>2.8</td>
<td>3.5</td>
<td>1.1</td>
<td>–</td>
</tr>
<tr>
<td>Lead Stearate</td>
<td>3.2</td>
<td>3.0</td>
<td>3.2</td>
<td>3.2</td>
<td>1.5</td>
<td>1.5</td>
<td>–</td>
<td>4.6</td>
<td>–</td>
</tr>
<tr>
<td>Sodium Barbiturate</td>
<td>1.0</td>
<td>0.6</td>
<td>3.0</td>
<td>3.0</td>
<td>–</td>
<td>1.0</td>
<td>1.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Oxamide</td>
<td>–</td>
<td>3.8</td>
<td>5.0</td>
<td>10.0</td>
<td>–</td>
<td>6.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calculated Flame Temp °F</td>
<td>2523</td>
<td>2715</td>
<td>2646</td>
<td>2747</td>
<td>2462</td>
<td>2460</td>
<td>2450</td>
<td>2480</td>
<td>1808</td>
</tr>
<tr>
<td>Heat of Explosion (Expt), cal/g</td>
<td>700</td>
<td>726</td>
<td>715</td>
<td>727</td>
<td>699</td>
<td>698</td>
<td>704</td>
<td>705</td>
<td>734</td>
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<td>Static Firing Data</td>
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</tr>
<tr>
<td>Pressure, psi</td>
<td>710</td>
<td>960</td>
<td>690</td>
<td>1138</td>
<td>1340</td>
<td>1130</td>
<td>910</td>
<td>960</td>
<td>650</td>
</tr>
<tr>
<td>Burning Time, sec</td>
<td>1.59</td>
<td>1.24</td>
<td>1.74</td>
<td>1.18</td>
<td>1.36</td>
<td>1.31</td>
<td>1.78</td>
<td>1.35</td>
<td>3.48</td>
</tr>
<tr>
<td>Mass Rate of Discharge, lb/sec</td>
<td>0.340</td>
<td>0.556</td>
<td>0.396</td>
<td>0.585</td>
<td>0.478</td>
<td>0.519</td>
<td>0.376</td>
<td>0.489</td>
<td>0.198</td>
</tr>
<tr>
<td>Light Attenuation, %</td>
<td>3.7</td>
<td>2.0</td>
<td>4.7</td>
<td>4.4</td>
<td>21.4</td>
<td>16.3</td>
<td>17.4</td>
<td>7.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Specific Attenuationc</td>
<td>10.9</td>
<td>3.6</td>
<td>11.8</td>
<td>7.3</td>
<td>44.8</td>
<td>31.4</td>
<td>46.3</td>
<td>16.1</td>
<td>12.6</td>
</tr>
</tbody>
</table>

a Standard type nitrocellulose base propellant
b Standard type ammonium nitrate composite propellant
c Specific attenuation = Light attenuation divided by Mass Rate of Discharge
Table 5  
Effect of Substitution of BTTN for TVOPA

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA/AA (95:5)</td>
<td>4.6</td>
<td>4.60</td>
<td>5.7</td>
<td>4.6</td>
</tr>
<tr>
<td>TVOPA</td>
<td>25.7</td>
<td>12.85</td>
<td>8.0</td>
<td>0.0</td>
</tr>
<tr>
<td>BTTN</td>
<td>0.0</td>
<td>12.85</td>
<td>23.8</td>
<td>25.7</td>
</tr>
<tr>
<td>HMX</td>
<td>48.5</td>
<td>48.50</td>
<td>60.1</td>
<td>48.5</td>
</tr>
<tr>
<td>AP</td>
<td>19.2</td>
<td>19.20</td>
<td>0.0</td>
<td>19.2</td>
</tr>
<tr>
<td>Diépoxydicyclohexyl carboxylate</td>
<td>1.5</td>
<td>1.50</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbon black</td>
<td>0.5</td>
<td>0.50</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Total Wt %</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

C*   
Cf   
Isp  

CH₄  
CO   
CO₂  
HCl  
H₂   
H₂O  
N₂   
NF   

5152  
1.562  
250.1  
0.010  
25.038  
8.732  
3.747  
18.310  
9.000  
20.545  
14.627  
5416  
1.575  
265.1  
—     
26.930  
11.636  
3.885  
14.398  
15.081  
12.904  
15.164  
5220  
1.565  
253.9  
0.010  
30.218  
9.812  
—     
22.130  
10.782  
22.612  
44.445

Calculated performance of typical propellants is shown in Table 5. The propellants employing ammonium perchlorate (AP) generate less smoke. RDX may be substituted for HMX in the formulation. Ethyl acrylate-acrylic acid copolymer (EA/AA) consists of from 90 to 96 parts acrylate and from 4 to about 10 parts acrylic acid. Those in Table 5 are about 95 parts ethyl acrylate and 5 parts acrylic acid. TVOPA is a difluoromethyl plasticizer for the EA/AA binders. Projected cost data for BTTN range from 1/4 to 1/6 that of TVOPA.

Sayles (Ref 82) also found that bis N-(trinitroethyl) nitramino ethane can be used as an oxidizer in EA/AA propellants to produce smokeless propellants. In these formulations it can replace HMX or HMX and AP. The results of this substitution on performance is shown in Tables 6 and 7.

Most expit smokeless propellants based upon the high-energy NF compds have been plagued with stability and ageing problems which results in poor shelf-life. Additionally, the cost projections on some of the ingredients results in an unreasonably high cost propellant.

B. Composite Propellants

Composite propellants, which are used almost entirely in rocket propulsion, normally contain a solid phase oxidizer combined with a polymeric fuel binder with a \(-\text{CH}_2-\text{CH}_2-\) structure. Practically speaking AP is the only oxidizer which has achieved high volume production, although ammonium nitrate (AN) has limited special uses such as in gas generators. Other oxidizers which have been studied more or less as curiosities include hydrazinium nitrate, nitronium perchlorate, lithium perchlorate, lithium nitrate, potassium perchlorate and others. Among binders, the most used are: polyurethanes, polybutadiene/acrylonitrile/acrylic acid terpolymers and hydroxy-terminated polybutadienes.

Modern polyurethane binders are derived by reacting polymeric diols with 2,4-toluene disiocyanate (TDI) and a bifunctional alcohol for cross-linking. By using glycols having molecular weights of 1000 to 4000 the shrinkage and heat of polymerization of the propellant as it is cured can be reduced to an optimum level to give the
Table 6  Effect of Substituting BT NEEDNA for HMX
in an EANF-Propellant Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acrylate-acrylic acid (95/S)</td>
<td>4.63</td>
</tr>
<tr>
<td>1,2,3-tris[1,2-bis(difluoroamino)-ethoxy] propane</td>
<td>25.68</td>
</tr>
<tr>
<td>HMX</td>
<td>48.56</td>
</tr>
<tr>
<td>bis[N-(trinitroethyl)nitramino]ethane</td>
<td>0.0</td>
</tr>
<tr>
<td>Ammonium Perchlorate</td>
<td>19.21</td>
</tr>
<tr>
<td>UNOX 221</td>
<td>1.44</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>0.48</td>
</tr>
<tr>
<td>Theoretical Performance</td>
<td></td>
</tr>
<tr>
<td>$C^*$ (fps)</td>
<td>5152</td>
</tr>
<tr>
<td>$C_f$</td>
<td>1.562</td>
</tr>
<tr>
<td>$I_sp$ (lb-sec/lb)</td>
<td>250.1</td>
</tr>
<tr>
<td>Exhaust Gas Composition (Mole Fractions)</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.00001</td>
</tr>
<tr>
<td>CO</td>
<td>0.25038</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.08732</td>
</tr>
<tr>
<td>H</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl</td>
<td>0.03747</td>
</tr>
<tr>
<td>HF</td>
<td>0.14627</td>
</tr>
<tr>
<td>$H_2$</td>
<td>0.18310</td>
</tr>
<tr>
<td>$H_2$O</td>
<td>0.09000</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.0001</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.20545</td>
</tr>
</tbody>
</table>

Table 7  Effect of Substituting BT NEEDNA for HMX and AP
in an EANF Propellant Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acrylate-acrylic acid (95/S)</td>
<td>4.63</td>
</tr>
<tr>
<td>1,2,3-tris[1,2-bis(difluoroamino)-ethoxy] propane</td>
<td>25.68</td>
</tr>
<tr>
<td>HMX</td>
<td>48.56</td>
</tr>
<tr>
<td>bis[N-(trinitroethyl)nitramino]ethane</td>
<td>0.0</td>
</tr>
<tr>
<td>Ammonium Perchlorate</td>
<td>19.21</td>
</tr>
<tr>
<td>UNOX 221</td>
<td>1.44</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>0.48</td>
</tr>
<tr>
<td>Theoretical Performance</td>
<td></td>
</tr>
<tr>
<td>$C^*$ (fps)</td>
<td>5152</td>
</tr>
<tr>
<td>$C_f$</td>
<td>1.562</td>
</tr>
<tr>
<td>$I_sp$ (lb-sec/lb)</td>
<td>250.0</td>
</tr>
</tbody>
</table>

required physical properties. The most significant variable in determining the mechanical properties of the polyurethane binder is the chemical structure of the polyol and the triol cross-linking agent. For instance, the physical properties of the 2,4-TDI/polypropylene glycol polymer are improved significantly by incorporating triethylene glycol, diethylene glycol, 2,5-hexanediol, ethylene glycol, polypropylene glycol, or polybutylene oxide in the binder formulations to cross-link the polymeric structure. Some typical polyurethane resin formulations are given in Table 8 (Ref 74). Among the curing catalysts for polyurethanes are cobaltic acetyl acetate, lead naphthenate, cobalt naphthenate and ferric acetyl acetate, with the latter being the most used.

Bimodal oxidizers are normally used to improve fluidity for mixing and casting. These consist of unground material which is in the range of 100 mesh and 30% ground oxidizer in the 10 to 30 micron size range. Two specific formulations are given below for an unalumined JPL X500 propellant in Table 9 (Ref 74). Uncatalyzed polyurethane propellants have unusually low burning rates. Copper chromate and ferric acetyl acetate are the more commonly used burning rate catalysts in polyurethane propellants, although ferric oxide, chromic oxide, ammonium dichromate, and organic ferrocenes are also effective (Ref 40). Lithium fluoride has been used as a burning rate depressant for polyurethane propellants (Ref 32).

Surface-active agents are introduced into polyurethane formulations to improve physical properties and to give increased fluidity during mixing. The polar residue of a suitable wetting agent adheres to the AP particles leaving the non-polar end as an effective lubricating film around the particle. Plasticizers are also added to improve physical properties such as elongation and brittleness, to improve castability, to lower the shrinkage and curing exotherm, and to reduce the interaction between resin binder and oxidizer. The variation in physical properties of JPL X500 with plasticizer and surface-active agent are shown in Table 10 (Ref 74).
### Table 8
Polyurethane Resin Formulae

<table>
<thead>
<tr>
<th>Components</th>
<th>JPL X500</th>
<th>JPL X360</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(wt %)</td>
<td>(mol)</td>
</tr>
<tr>
<td>Diols</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypropylene glycol 2025&lt;sup&gt;1&lt;/sup&gt;</td>
<td>79.7</td>
<td>0.364</td>
</tr>
<tr>
<td>Polypropylene glycol 3000&lt;sup&gt;1&lt;/sup&gt;</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Polypropylene glycol 150&lt;sup&gt;1&lt;/sup&gt;</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Triethylene glycol</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Diisocyanate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene diisocyanate&lt;sup&gt;2&lt;/sup&gt;</td>
<td>15.8</td>
<td>1.000</td>
</tr>
<tr>
<td>Triols</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexane Triol&lt;sup&gt;3&lt;/sup&gt;</td>
<td>4.1</td>
<td>0.335</td>
</tr>
<tr>
<td>Triol 230&lt;sup&gt;4&lt;/sup&gt;</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Triisopropanolamine</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Curing catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferric acetyl acetonate</td>
<td>0.35</td>
<td>—</td>
</tr>
<tr>
<td>Ratio of isocyanate to alcohol</td>
<td>1.15</td>
<td>—</td>
</tr>
<tr>
<td>Polymer weight per mole of cross-linking agent (gm/gm mol)</td>
<td>3280</td>
<td>—</td>
</tr>
</tbody>
</table>

<sup>1</sup> Polyether diols

<sup>2</sup> 2,4-toluene diisocyanate

<sup>3</sup> 1,2,6-hexane triol

<sup>4</sup> HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>C(CH<sub>3</sub>)(CH<sub>2</sub>OH)CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>OH

### Table 9
Composition of JPL X500

<table>
<thead>
<tr>
<th>Wt % of Propellant</th>
<th>70% Oxidizer</th>
<th>80% Oxidizer</th>
<th>Wt % of Binder&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ground&lt;sup&gt;a&lt;/sup&gt;</td>
<td>21.0</td>
<td>24.0</td>
<td>—</td>
</tr>
<tr>
<td>ground&lt;sup&gt;a&lt;/sup&gt;</td>
<td>49.0</td>
<td>56.0</td>
<td>—</td>
</tr>
<tr>
<td>Polypropylene glycol 2025 (PPG)</td>
<td>23.9</td>
<td>15.9</td>
<td>79.6</td>
</tr>
<tr>
<td>Ferric acetyl acetonate (FAA)</td>
<td>0.1</td>
<td>0.08</td>
<td>0.4</td>
</tr>
<tr>
<td>Tolylene diisocyanate (TDI)</td>
<td>4.8</td>
<td>3.2</td>
<td>16.0</td>
</tr>
<tr>
<td>1,2,6-Hexanetriol (HT)</td>
<td>1.2</td>
<td>0.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> A bimodal oxidizer system is used in this propellant, consisting of 30% ground and 70% unground ammonium perchlorate

<sup>b</sup> Weight of plasticizer and/or surfactant used is subtracted from weight of binder in propellant
Table 10
Variation of Physical Properties of JPL X500 Propellant with Addition of a Plasticizer and a Surface-Active Agent

<table>
<thead>
<tr>
<th>Compound Added</th>
<th>Tensile Strength (psi) at</th>
<th>Elongation (%) at</th>
<th>Initial Modulus (psi) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-40°F  80°F  160°F</td>
<td>-40°F  80°F  160°F</td>
<td>-40°F  80°F  160°F</td>
</tr>
<tr>
<td>None</td>
<td>1,355  155  130</td>
<td>5.3   11.2  6.6</td>
<td>79,000  3,840  4,000</td>
</tr>
<tr>
<td>Ionol (1%)</td>
<td>934   120   76</td>
<td>12.0   12.6  6.4</td>
<td>41,500  2,765  3,235</td>
</tr>
<tr>
<td>Dioctyl azelate (10%)</td>
<td>310   80   61</td>
<td>37.0   16.2  11.0</td>
<td>3,095  1,120  1,145</td>
</tr>
<tr>
<td>Ionol (1%) and dioctyl azelate (10%)</td>
<td>263   69   49</td>
<td>44.0   14.0  8.4</td>
<td>2,945  985   735</td>
</tr>
</tbody>
</table>

a Composition: ammonium perchlorate 70% and polyurethane binder 30% (includes plasticizer and/or surfactant weight)

Another class of hydrocarbon binders used in propellants are the carboxy-terminated polybutadiene polymers which are cross-linked with either tris[1-(2-methyl)aziridinyl] phosphine oxide (MAPO) or combinations with phenyl bis[1-(2-methyl)aziridinyl] phosphine oxide (Phenyl MAPO). Phenyl MAPO is a difunctional counterpart of MAPO which makes possible chain extension of polymers with two carboxylic acid groups. A typical propellant formulation with ballistic properties is in Table 11 (Ref 83).

Another class of composites includes those using hydroxy-terminated polybutadienes cross-linked with toluene diisocyanate as binders. The following simplified equations illustrate typical reactions involved in binder formation

Table 11
Carboxy-Terminated Polybutadiene
Propellant Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% by wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butarez CTL (carboxy-terminated polybutadiene polymer)</td>
<td>8.28</td>
</tr>
<tr>
<td>MAPO</td>
<td>0.31</td>
</tr>
<tr>
<td>Isodecylpolargonate</td>
<td>5.41</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>64.00</td>
</tr>
<tr>
<td>Copper chromite</td>
<td>1.00</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>21.00</td>
</tr>
<tr>
<td>Burning rate (1000psi, 70°F, inch/sec)</td>
<td>0.53</td>
</tr>
<tr>
<td>Specific impulse (lbf·sec/lbm)</td>
<td>232.3</td>
</tr>
</tbody>
</table>

Table 12
Hydroxy-Terminated Polybutadiene
Propellant Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% by wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxy-terminated polybutadiene</td>
<td>7.82</td>
</tr>
<tr>
<td>Toluene diisocyanate</td>
<td>0.46</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>0.38</td>
</tr>
<tr>
<td>Dioctyl azelate</td>
<td>4.48</td>
</tr>
<tr>
<td>sym-Di-beta-naphthyl-p-phenylenediamine</td>
<td>0.20</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>68.00</td>
</tr>
<tr>
<td>Powdered aluminum</td>
<td>18.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.00</td>
</tr>
</tbody>
</table>
diene with acrylic acid (PABA) and terpolymers of 1,3-butadiene, acrylic acid, and acrylonitrile (PBAN). Formulations using these binder materials are given in Tables 13 and 14 (Refs 32 & 63).

Without the influence of burning rate catalysis most of these hydrocarbon propellants have similar burning rates and ballistic behavior. They may differ significantly in mechanical properties, particularly as a function of temp. Most hydrocarbon-based composites are used in larger rockets because of their ease of fabrication and high specific impulse. Polaris first and second stages, the Titan 3C booster rocket and Minuteman are all powered with composite propellants.

A relatively new class of fluorocarbon composite propellants with relatively high specific impulse and a high density impulse have been tested as booster rockets for 5-inch projectiles.

**Table 15**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>A 10 B 5 C 8 D 8</td>
</tr>
<tr>
<td>Viton A</td>
<td>A 15 B 15 C 12 D 12</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>A 55 B 65 C - D -</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>A 20 B - C 20 D 5</td>
</tr>
<tr>
<td>Beryllium</td>
<td>A - B 15 C - D -</td>
</tr>
<tr>
<td>Nitronium perchlorate</td>
<td>A - B - C 45 D 50</td>
</tr>
<tr>
<td>Triaminoguanidine</td>
<td>A - B - C 15 D -</td>
</tr>
<tr>
<td>Aluminum hydride</td>
<td>A - B - C 25 D -</td>
</tr>
</tbody>
</table>

**Table 14**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% by wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBAN terpolymer</td>
<td>10.886</td>
</tr>
<tr>
<td>Epoxy curing system</td>
<td>5.914</td>
</tr>
<tr>
<td>Ammonium perchlorate (unground)</td>
<td>44.20</td>
</tr>
<tr>
<td>Ammonium perchlorate (ground 11 u)</td>
<td>24.00</td>
</tr>
<tr>
<td>Aluminum (Re 1-131)</td>
<td>15.00</td>
</tr>
<tr>
<td>Burning rate, inch/sec at 1000 psi</td>
<td>0.33</td>
</tr>
<tr>
<td>Burning rate exponent, n</td>
<td>0.34</td>
</tr>
</tbody>
</table>

The compons are based upon a copolymer of vinylidene fluoride and perfluoropropylene (Viton A) with polytetrafluoroethylene (Teflon) and various metals and oxidizers. A number of extrudable formulations are listed in Table 15 (Ref 57). The major advantages claimed for these propellants are high density impulse, compatibility with highly energetic propellant ingredients and resistance to high centrifugal forces.

Modification of the burning rates, pressure exponents, and temp coefficients of burning rate of the fluorocarbon composites has been accomplished with copper, lead, tin, sodium, ammonium and potassium fluoborates; sodium, potassium, lithium, lead, copper and calcium fluorides; potassium and ammonium dichromate; lead and zinc stearate; caesium carbonate; potassium and ammonium sulfate; copper chromite; oxides of magnesium, copper and manganese; boron; zinc dust; and carbon black (Ref 75).

**C. High Energy Solid Propellants**

To achieve higher energy in solid propellants the most notable advances were achieved with the addition of aluminum and beryllium to both double-base and composite propellants. Energy in this case is commonly equated to high specific impulse. Later developments added aluminum hydride and beryllium hydride to this list. In Table 16, the specific impulse performance of pro propelants using AP with various metals and hydrides is compared to those systems without these additives (Ref 43).

There are stability problems with most of the metal additives other than aluminum, although
Table 16
Effect of Metal Additives on Specific Impulse of Ammonium Perchlorate Propellants

<table>
<thead>
<tr>
<th>Fuel</th>
<th>wt % fuel</th>
<th>wt % additive</th>
<th>I_sp (lbf-sec/lbm)</th>
<th>Chamber Temp, °K</th>
<th>Density g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₂</td>
<td>15</td>
<td>0</td>
<td>246.5</td>
<td>2950</td>
<td>1.66</td>
</tr>
<tr>
<td>Double-base</td>
<td>40</td>
<td>0</td>
<td>250.7</td>
<td>3051</td>
<td>1.73</td>
</tr>
<tr>
<td>-CH₂</td>
<td>15</td>
<td>Al (19%)</td>
<td>264.1</td>
<td>3179</td>
<td>1.74</td>
</tr>
<tr>
<td>Double-base</td>
<td>45</td>
<td>Al (20%)</td>
<td>263.5</td>
<td>3760</td>
<td>1.80</td>
</tr>
<tr>
<td>-CH₂</td>
<td>15</td>
<td>AlH₃ (34%)</td>
<td>274.2</td>
<td>2546</td>
<td>1.53</td>
</tr>
<tr>
<td>Double-base</td>
<td>40</td>
<td>AlH₃ (28%)</td>
<td>285.2</td>
<td>3417</td>
<td>1.61</td>
</tr>
<tr>
<td>-CH₂</td>
<td>15</td>
<td>Be (12%)</td>
<td>285.6</td>
<td>3172</td>
<td>1.66</td>
</tr>
<tr>
<td>Double-base</td>
<td>40</td>
<td>Be (16.8%)</td>
<td>279.3</td>
<td>4071</td>
<td>1.72</td>
</tr>
<tr>
<td>-CH₂</td>
<td>20</td>
<td>BeH₂ (25%)</td>
<td>304.0</td>
<td>2644</td>
<td>1.14</td>
</tr>
<tr>
<td>Double-base</td>
<td>50</td>
<td>BeH₂ (20%)</td>
<td>313.8</td>
<td>3154</td>
<td>1.28</td>
</tr>
</tbody>
</table>

this is not as serious a problem with beryllium as with the two hydrides AlH₃ and BeH₂. All three induce gassing in most formulations with resulting porosity and higher than normal burning rates. The other disadvantage, for most military uses, is the lower density achieved with hydride formulations. For the most part, the higher velocity, and therefore longer ranges, are achieved with the higher density impulse propellants. The applicable equation is

\[ BV = \frac{g_0}{I_sp} \ln(1/1-MF) \]

where \( MR = 1/1-MF \), \( MR = \text{mass ratio} \); \( MF = \text{mass fraction} \); \( g_0 = \text{gravity constant} \); \( I_sp = \text{specific impulse, lbf-sec/lbm} \), and \( BV = \text{boost velocity, ft/sec} \). The mass fraction is defined as the ratio of the propellant mass to the total mass of the rocket. Thus the effect of high propellant density is to increase the mass ratio and therefore maximize the boost velocity. Since the reduction of metal parts and payload weights pays diminishing returns, the other alternative is to increase the specific impulse of the propellant in order to achieve higher performance. A large effort has been exerted toward this end thru research into more energetic oxidizers and binders.

Hydrazinium diperchlorate (HP₂) is one of the higher energetic oxidizers considered for use in composite solid propellants with hydrocarbon binders. Its other advantages include high density, high burning rate, and moderate projected cost. Its shortcomings include relatively poor stability to vibrational and thermal shock when formulated into the usual polymeric fuel binders. Because of its poor shock sensitivity, batch size and motor size are limited to exp'tl research quantities. Stabilization of HP₂ has been effected by adding from 0.1 to 10% by weight of ethylenediamine tetraacetic acid (EDTA) to HP₂ in aq or non-aq solns prior to the final crysn which precedes the final drying step (Ref 55). In general, many chelating agents have been found to be effective in stabilization of HP₂. Wall (Ref 58) was able to incorporate HP₂ into composite formulations using such stabilizers as N,N'-diphenyl-p-phenylenediamine, N,N'-ditolyl-p-phenylenediamine, N,N'-dixylyl-p-phenylenediamine and many others containing sulfur and nitrogen usually bound in a heterocyclic ring and with weakly basic characteristics. Proplnt compns with better stability, physical properties, ballistic performance and lower cost were formulated as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilizer</td>
<td>0.5 – 4.0</td>
</tr>
<tr>
<td>HP₂</td>
<td>60 – 80</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>0 – 20</td>
</tr>
<tr>
<td>Carboxy-terminated polybutadiene binder</td>
<td>15 – 25</td>
</tr>
<tr>
<td>Aluminum or beryllium powder</td>
<td>10 – 20</td>
</tr>
</tbody>
</table>

Hydroxyammonium perchlorate is another high energy oxidizer with stability, high impulse and high density claimed to be an improvement over AP (Ref 59). Several preferred proplnt compns incorporating this oxidizer are listed in Table 17.
Table 17

Composite Propellants Containing Hydroxylammonium Perchlorate

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxylammonium perchlorate</td>
<td>64.00</td>
<td>64.00</td>
<td>65.00</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>18.00</td>
<td>18.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Hydroxy-terminated copolymer of butadiene and styrene</td>
<td>15.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Epoxy, ERL-2795</td>
<td>2.60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxy-terminated polybutadiene</td>
<td>-</td>
<td>15.08</td>
<td>-</td>
</tr>
<tr>
<td>Epoxide 201</td>
<td>-</td>
<td>2.92</td>
<td>-</td>
</tr>
<tr>
<td>Castor oil</td>
<td>-</td>
<td>-</td>
<td>12.03</td>
</tr>
<tr>
<td>Toluene diisocyanate</td>
<td>-</td>
<td>-</td>
<td>2.97</td>
</tr>
<tr>
<td>Delivered I&lt;sub&gt;SP&lt;/sub&gt;, lbf·sec/lbm at 1000psi</td>
<td>246</td>
<td>254</td>
<td>-</td>
</tr>
<tr>
<td>Burning rate, inch/sec at 1000psi</td>
<td>0.60</td>
<td>0.30</td>
<td>0.82</td>
</tr>
<tr>
<td>Burning rate exponent, n</td>
<td>0.49</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>Density, lb/inch&lt;sup&gt;3&lt;/sup&gt;</td>
<td>-</td>
<td>0.067</td>
<td>-</td>
</tr>
</tbody>
</table>

NC-based composite propellants have also been formulated with high energy ingredients, although in many cases the NC is replaced with other expl plasticizers. Reinhart (Ref 62) has developed a series of plastisol-NC propellants using pentaerythritol trinitrate (Petrin) and/or trimethylolmethane trinitrate (TMETN) as plasticizers. Table 18 gives examples of these formulations and their ballistic properties. Other high energy additives such as HMX and TNEC (trinitroethyl-orthocarbonate) were also used with this binder as indicated in Table 19. Measured specific impulse at 1000psi ranged from a low of 227 to a high of 274 lbf·sec/lbm for these variants.

Beryllium hydride has been used by Butts (Ref 70) in combination with a specific nitrate ester plasticizer for NC selected from the group consisting of nitroisobutanetriol trinitrate (NIBTN), 2,2-dinitropropanediol dinitrate (DNPDN) and nitroethylnitrate (TNEN). Co-plasticizers which are used include diethylene glycol dinitrate (DEGDN) or ethyleneglycol dinitrate (EGDN). Formulations with BeH<sub>2</sub> are in Table 20. The formulation in Example 2 has a theoretical I<sub>SP</sub> of 301 lbf·sec/lbm and a non-equilibrium flame temp of 2600°F.

Table 18

<table>
<thead>
<tr>
<th>Composition and Properties</th>
<th>Example</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td>1</td>
<td>23.5</td>
<td>27.0</td>
<td></td>
</tr>
<tr>
<td>Aluminum, atomized</td>
<td>21.5</td>
<td>20</td>
<td>21.5</td>
<td>23.0</td>
</tr>
<tr>
<td>Nitrocellulose (12.6% N)</td>
<td>16.2</td>
<td>17.1</td>
<td>19.0</td>
<td>14.3</td>
</tr>
<tr>
<td>PETRIN</td>
<td>39.9</td>
<td>27.0</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethyl centralite</td>
<td>0.9</td>
<td>0.9</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Burning rate, 70°F</td>
<td>0.45</td>
<td>0.37</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>1000psi, inch/sec</td>
<td>0.6</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Pressure exponent</td>
<td>1675</td>
<td>1521</td>
<td>1675</td>
<td>1741</td>
</tr>
<tr>
<td>Heat of Explosion, cal/g</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Tg, mmHg/min</td>
<td>15</td>
<td>14</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Impact sensitivity, 50% point, cm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table 19

<table>
<thead>
<tr>
<th>Composition and properties</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder type a</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>HMX, 100 avg percent</td>
<td>37</td>
<td>22</td>
<td>20</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>TNEOC, percent</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium perchlorate, percent</td>
<td>18</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum, atomized, percent</td>
<td>13</td>
<td>16</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Burning rate, 70°F and 1000 psi, inch/sec</td>
<td>0.35</td>
<td>0.15</td>
<td>0.22</td>
<td>0.34</td>
<td>0.3</td>
</tr>
<tr>
<td>Pressure exponent</td>
<td>1.0</td>
<td>0.9</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Heat of explosion, cal/g</td>
<td>1,057</td>
<td>908</td>
<td>1,079</td>
<td>1,433</td>
<td>1,490</td>
</tr>
<tr>
<td>Taitani, MM Hg/min</td>
<td>1.4</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Impact sensitivity, 50% point, cm</td>
<td></td>
<td>33b</td>
<td></td>
<td>25b</td>
<td></td>
</tr>
</tbody>
</table>

a See the following table:

**Binder formulations, weight percent:**
- Nitrocellulose (12.6% N) 38 28.5
- Petrin 39 70
- Dibutyl phthalate 20
- Adiponitrile 1
- Ethyl centralite 2 1.5

b Uncured

### Table 20

<table>
<thead>
<tr>
<th>Plastic Binder</th>
<th>Example 1</th>
<th>9–14%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Plasticizer</td>
<td></td>
<td>3–15%</td>
</tr>
<tr>
<td>Oxidizer</td>
<td></td>
<td>0–35%</td>
</tr>
<tr>
<td>Beryllium Hydride Fuel</td>
<td>15–24%</td>
<td></td>
</tr>
<tr>
<td>Nitro-Nitrat Ester Plasticizer</td>
<td>10–40%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>Diethyleneglycol dinitrate</td>
</tr>
<tr>
<td>Ammonium Perchlorate</td>
</tr>
<tr>
<td>Beryllium Hydride</td>
</tr>
<tr>
<td>Nitrosobutanetriol Trinitrate (NBPTN)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>Diethyleneglycol dinitrate</td>
</tr>
<tr>
<td>Ammonium Perchlorate</td>
</tr>
<tr>
<td>Beryllium Hydride</td>
</tr>
<tr>
<td>2,2-dinitropropanediol dinitrate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>Ethyleneglycol dinitrate</td>
</tr>
<tr>
<td>Potassium perchlorate</td>
</tr>
<tr>
<td>Beryllium Hydride</td>
</tr>
<tr>
<td>Nitroethyl Nitrate (TEN)</td>
</tr>
</tbody>
</table>

### Table 21

<table>
<thead>
<tr>
<th>Propellant Composition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>weight per cent</td>
</tr>
<tr>
<td>N</td>
<td>NC</td>
</tr>
<tr>
<td>1</td>
<td>12.5</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
</tr>
<tr>
<td>3</td>
<td>11.25</td>
</tr>
<tr>
<td>4</td>
<td>12.5</td>
</tr>
<tr>
<td>5</td>
<td>11.25</td>
</tr>
<tr>
<td>6</td>
<td>11.25</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>8.75</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>8.75</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>8.75</td>
</tr>
</tbody>
</table>

1 nitrocellulose
2 trimethylethane trinitrate
3 hydrazine nitroformate
Klunisch (Ref 72) has incorporated hydrazinium nitroformate and aluminum hydride in plastisol NC formulations which cure at room temp without undesirable gas formation. A number of such formulations and calculated ballistic results are given in Table 21. Although these are attractive propellants from the standpoint of potential energy, their impact sensitivity was not described. Similar plastisol binder propellants in Table 18 were sensitive enough to impact to warrant extreme caution in processing into rockets.

Flynn (Ref 73) continued the trend of using the rather inert plastisol NC binder to synthesize the propellants containing aluminum hydride and nitrocellulose shown in Table 22. In this case, the stability of nitrocellulose perchlorate, in terms of gassing and friction sensitivity is enhanced by surface-coating it with from 7 to 8 percent of a polymeric dichlorostyrene. For optimum physical stability during formulation, curing, and storage, substantially all traces of moisture and acids must be removed from all ingredients. Furthermore, these operations should be carried out in an inert atm of nitrogen or argon. This well illustrates the extremes in technology which are required to safely handle many of these proposed high-energy ingredients

<table>
<thead>
<tr>
<th>Run No</th>
<th>Propellant Composition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrocellulose</td>
<td>TEMPn^2</td>
</tr>
<tr>
<td></td>
<td>weight per cent</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>11.25</td>
<td>33.75</td>
</tr>
<tr>
<td>2</td>
<td>11.25</td>
<td>33.75</td>
</tr>
<tr>
<td>3</td>
<td>11.25</td>
<td>33.75</td>
</tr>
<tr>
<td>4</td>
<td>8.75</td>
<td>26.25</td>
</tr>
<tr>
<td>5</td>
<td>8.75</td>
<td>26.25</td>
</tr>
<tr>
<td>6</td>
<td>8.75</td>
<td>26.25</td>
</tr>
</tbody>
</table>

1) Nitrocellulose
2) Trimethylethylene trinitrate
3) Nitronium perchlorate

Experimentally, Flynn (Ref 73a) has tested plastisol NC composite propellants containing beryllium and triaminoguanidinium hydrazinium diazide in a closed bomb and measured the high specific impulses indicated in Table 23. Other formulations containing the ingredients aluminum and hydrazine nitroformate resulted in high calculated impulses as the data in Table 24 show.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Propellant Composition</th>
<th>Combustion Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrocellulose</td>
<td>AI (% by weight)</td>
</tr>
<tr>
<td>1</td>
<td>40^1</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>40^1</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>35^1</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>40^2</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>–</td>
</tr>
</tbody>
</table>

1) 25 parts by weight plasticized grade nitrocellulose, 55 parts by weight trimethylethylene trinitrate, 15 parts by weight diethylene glycol dinitrate, 5 parts by weight toluene disiocyanate
2) 25 parts by weight plasticized grade nitrocellulose, 60 parts by weight trimethylethylene trinitrate and 15 parts by weight triethylene glycol dinitrate
3) ammonium perchlorate
4) triaminoguanidinium hydrazinium diazide
Table 24

Propellant Composition

<table>
<thead>
<tr>
<th>Run No</th>
<th>NC(^1)</th>
<th>TMETN(^2)</th>
<th>Al</th>
<th>Be</th>
<th>Alth</th>
<th>AP(^4)</th>
<th>HNF(^5)</th>
<th>Comb Temp</th>
<th>Specific Impulse I(_{sp}) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.5</td>
<td>27.5</td>
<td>17.9</td>
<td>-</td>
<td>29.2</td>
<td>17.9</td>
<td>-</td>
<td>3407</td>
<td>275.6</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>25.0</td>
<td>15.0</td>
<td>-</td>
<td>31.5</td>
<td>23.5</td>
<td>-</td>
<td>3379</td>
<td>274.5</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>27.5</td>
<td>18.0</td>
<td>-</td>
<td>32.5</td>
<td>14.5</td>
<td>-</td>
<td>3236</td>
<td>272.3</td>
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<tr>
<td>4</td>
<td>5.0</td>
<td>25.0</td>
<td>18.0</td>
<td>-</td>
<td>35.0</td>
<td>17.0</td>
<td>-</td>
<td>3243</td>
<td>273.2</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>25.0</td>
<td>21.0</td>
<td>-</td>
<td>31.5</td>
<td>17.5</td>
<td>-</td>
<td>3263</td>
<td>270.3</td>
</tr>
<tr>
<td>6</td>
<td>10.0</td>
<td>30.0</td>
<td>23.0</td>
<td>-</td>
<td>18.0</td>
<td>19.0</td>
<td>-</td>
<td>3617</td>
<td>272.0</td>
</tr>
<tr>
<td>7</td>
<td>10.0</td>
<td>30.0</td>
<td>18.0</td>
<td>-</td>
<td>12.0</td>
<td>30.0</td>
<td>-</td>
<td>3745</td>
<td>271.4</td>
</tr>
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<td>8</td>
<td>5.0</td>
<td>25.0</td>
<td>19.0</td>
<td>-</td>
<td>21.0</td>
<td>30.0</td>
<td>-</td>
<td>3677</td>
<td>274.7</td>
</tr>
<tr>
<td>9</td>
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<td>30.0</td>
<td>21.0</td>
<td>-</td>
<td>12.0</td>
<td>-</td>
<td>27.0</td>
<td>3789</td>
<td>278.2</td>
</tr>
<tr>
<td>10</td>
<td>10.0</td>
<td>30.0</td>
<td>19.0</td>
<td>-</td>
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<td>-</td>
<td>35.0</td>
<td>3744</td>
<td>295.8</td>
</tr>
</tbody>
</table>

\(^1\) Nitrocellulose  
\(^2\) Trimethylolethane trinitrate  
\(^3\) Triaminoguanidinium hydrazinium diazide  
\(^4\) Ammonium perchlorate  
\(^5\) Hydrazine Nitroformate

This review of the state-of-the-art in high-energy propellant technology is not intended to be all-inclusive, but it is intended to give typical examples of the compounds under consideration and the problems in sensitivity and stability which have been encountered.

D. Configurations

Missions flown by solid propellant rockets are predetermined or programmed by the design of the burning surface. Normally the propellant is case-bonded to the motor case or otherwise inhibited so that it burns only on the internal surface. The simplified approach is to assume that the burning surface recedes in burning parallel layers in a direction perpendicular to the surface itself. For rocket motors where combustion pressures do not normally exceed 2000psia, the propellant burning rate may be given as a function of the chamber press by the following empirical equation:

\[ r = aP_c^n \]

where \( r \) = burning rate (inch/sec), \( P_c \) = chamber press (psi), \( n \) = burning rate exponent, and \( a \) = a constant. Thus the propellant mass flow rate (neglecting erosion) becomes

\[ \dot{m} = A_s \rho a P_c^n \]

where \( \dot{m} \) = propellant mass flow rate (lb/sec), \( A_s \) = burning surface area (sq inches), \( \rho \) = propellant density (lb/cu inch). For stable operation, the mass flow rate must equal the mass discharge rate at the nozzle which is

\[ \dot{m} = C_p A_t \]

where \( C_D \) = nozzle discharge coefficient and \( A_t \) = nozzle throat area (sq inch), and therefore the equilibrium chamber press by this simplified analysis will be

\[ P_c = \left( \frac{A_s \rho a}{C_D A_t} \right)^{1/1-n} \]

Since the thrust (F) is given by

\[ F = C_F C_p A_t = C_F \left( \frac{A_s \rho a}{C_D A_t} \right)^{1/1-n} A_t \]

where \( C_F \) = thrust coefficient, the design of the internal propellant grain configurations determines the thrust level required for the mission. Some typical star grain configurations give the thrust versus time curves shown in Figure 1 (Ref 28)
Fig 1 Grain Configurations and Thrust-Time Records

**Erosion of Gun Barrels**

One of the earliest uses of SP, and a use that continues to be important even at present, was in propelling projectiles out of gun barrels. The heat and combustion products of the propelling SP charge can have a deleterious effect on the bore of a gun barrel. This breaking down and wearing away of bore metal is called erosion. Gun barrel erosion has been discussed at some length in Vol 5, E112–20 and D1536.

Since the publication of these articles no major breakthroughs in erosion, or rather erosion prevention, have been made. However, several patents claiming methods and means of minimizing gun barrel erosion have appeared recently. These are abstracted below:

**Additives for reduction of gun wear.** M. Roth, USP 3282215 (1966) & CA 66, 30648 (1967). An additive is added to cartridges and shells to reduce erosion in gun barrels. The additive may be CaSO₄, CaCO₃, TiO₂ or combinations dispersed in amounts of 10–90 weight % in a paraffin wax, which is impregnated into rayon yarn containing a melamine resin and is then wrapped around the propellant. Other additives include ZnO, ZnS and Sb₂O₃; and Mg, Sr, and Ba sulfates, carbonates, and oxides.

**Gunpowder erosion reducer.** J.P. Picard, FrP 1526983 (1968) & CA 71, 31968 (1969). Hot gas erosion in the barrel of a firearm is reduced to about 0.8% of its usual value by incorporation into or on the surface of the propellant of 1–5% 3–60 micron, cheap, plentiful inorganic materials such as SiO₂ and MgO separately, or preferably, in a wt % ratio of 45–65/20–55, or of talc, with the propellant, by coating the propellant grains, or by application of a sheet of the additive dispersed in a carrier such as synthetic fibers, foamed polyurethane, or paraffin or micro-crystalline wax (mp 50–120°) placed between propellant charge and projectile. Mode of application is diagrammatically detailed. Thus, in firing tests of a 105mm rifle using M2 propellant, the loss of erosion with each firing averaged 24.1 mgs. When rayon fabric (95–120/g/m²) coated with a layer ~1.6mm thick of a mixt of 55% paraffin and 45% SiO₂, a 65:35 SiO₂–MgO mixt, or Calif, NY, or Montana talc was placed ahead of the propellant, the loss dropped to 0.2mg/firing.

**Gun barrel wear reduction additives.** D.E. Jacobson & S.Y. Ek, USP 3403625 (1968) & CA 70, 13144 (1969). Wear due to the erosion of a metal surface, such as the inside of a gun barrel, thru contact with hot rapidly flowing gases is reduced to one-tenth or less of its normal value without substantial change in firing characteristics by incorporating into a propellant charge powdery inorganic material at about or in front of the position of the said charge prior to the firing thereof, which becomes suspended in the hot gases emanating from the charge upon firing and coats the barrel with an erosion-resistant layer. The powdery inorganic material, such as sulfides or oxides of Ti, Ta, W, V, Zn or Nb is admixed with approx an equal weight of a carbonaceous material such as paraffin, ozokerite, China-Lack paint, NC, or lubricating grease, the molten mixt applied to the inner surface of a rayon, silk, or nylon wrap in an amount equal to 0.05–30% (preferably about 3%) of the weight of the propellant charge, and the treated fabric wrapped around the charge. Preferably, the inorganic additive mixt is largely at the forward portion of the charge. Details of application are described with the aid of 12 figs. Thus, wraps having a layer about 50mm long and 0.5mm thick of a 50:50 mixt of paraffin and WO₃, Nb₂O₅, TiO₂, or Ta₂O₅, a 60:40 paraffin-ZnO,
or a 67:33 paraffin-Zn mixt in conjunction with the charge of a 37mm cannon resulted in reduction in barrel wear to less than 5% of its value in the absence of the additive.

*Gun barrel wear reduction additives.* D.E. Jacobson & S.Y. Ek, USP 3404626 (1968) & CA 70, 13145 (1969). ZrO₂, HfO₂, ZrOCl₂, 8H₂O, or K₂TiF₆.H₂O is substituted for the oxides or sulfides described in USP 3403625 above.


A variant of gun barrel erosion, namely rocket nozzle erosion, is discussed in the following abstract:

*Role of carbon gas reactions in the erosion of rocket nozzles.* G.A. Heath & R.W. Thackray, AGARD Conf Proc, 52, 28 (1970) & CA 73, 100602 (1970). While graphites had excellent physical and mechanical properties in uncooled rocket nozzles, they underwent corrosion from chemical reactions with gaseous combustion products. The reactivity of the nozzle surface rose progressively with the temp during rocket operation. Up to 1600°C, the erosion agreed with that predicted by a chemical rate-control mechanism. Above 1600°C, the predicted values were too high because of boundary layer effects which hindered transfer of reactants from the free stream to the surface. Highly anisotropic pyrolytic graphite, which had the lowest reactivity to oxidizing gases and the highest resistance to erosion in nozzles, may be used to advantage in practical designs.

IV. Production Methods of Representative Propellants

A. Technology

NC-base proplnts are categorized as single-base, double-base, or triple-base proplnts. The manufacturing processing steps for the proplnts are distinct from those employed for making the final rocket motors. However, when the final product is a gun propint, it normally goes thru only the initial manufacturing step. Smokeless powder for shells and casting powder for rocket motors may be made either by a solvent or solventless extrusion process (Ref 33). In the solvent process, NC fibers in water- or alcohol-
cizer, usually NG, desensitizing agents and other liquid ingredients, is then introduced into the mold. Upon curing at about 140°F the solvent causes the individual grains to coalesce and form a single proplnt grain within the mold (Ref 33).

Composite proplnts are normally mixed in heavy-duty sigma-blade mixers or vertical mixers which impart the necessary work to the mixt required to ensure a homogeneous dispersion of binder and oxidizer. Several continuous mixing plants have also been constructed utilizing the Baker-Perkins continuous extrusion machine to achieve the required dispersion of liquids and solids. The batch machines are favored for those plants where production runs are short and proplnt formulation changes are frequent. The continuous processes are favored for high-volume production runs of the same formulation. Elaborate continuous feeding mechanisms are required to maintain formulations within specification ranges. For the most part, the production volume rarely justifies the capital expenditure required for continuous mixing processes, and today the volume of proplnts which are mixed by continuous processes is small.

Batch mixing of composite proplnts begins with the preparation of a premix containing all ingredients except the AP and curing agent. This reasonably low viscosity premix can be prepared in rather large batches which are sampled for quality control of ingredient proportions. The proper weight of heated premix is then charged to the mixer which is operated remotely as the oxidizer is charged and the proplnt is heated to temps in the range of 150–60°F. Oxidizer preparation consists of drying to low moisture, grinding a portion to a size in the range of 10–12 microns and blending. Upon completion of oxidizer addition, the curing agent is added. The mix cycle is adjusted to give a homogeneous proplnt with uniform ballistic properties and a suitable casting viscosity. After mixing is completed, the change-can mixing bowl is transported to the casting area where the proplnt is cast under vacuum into motor cases lined with inhibitor for curing. Typical curing cycles for polyurethanes are in the range of 5 days at 140°F. For carboxy-terminated polybutadiene binders, curing times of 3 days at 165°F are common. Upon completion of curing, the mandrel which forms the burning perforation is stripped from the rocket motor and finish trimming or inhibiting, if required, is performed.

In composite proplnt processing, the mixing process has always been the highest risk area and numerous mixers have been damaged or destroyed by fires and expls. When the industry came into being, the horizontal bread-dough mixers predominated and the bearings were submerged in proplnt where friction could cause ignition. The final solution to this problem was the introduction of the vertical batch mixers with overhead bearings and change-can mixing bowls to achieve higher productivity. As solid rocket sizes increased, mixers in the 150-gallon and 300-gallon sizes were introduced. A second generation mixer with a capacity of 500 gallons (10,000 lb capacity) is in operation at United Technology Center where it produces proplnt for large booster rockets each containing several hundred thousand pounds of composite proplnt. This large vertical mixer is single-shafted using a single helix for an impeller (Ref 41).

Another continuous mixing procedure being employed for the more sensitive double-base proplnts utilizes an inert and insoluble carrier to convey the proplnt ingredients thru the mixer (Ref 23). First the oxidizer and other solid ingredients, including metal powders, are each dispersed in a suitable carrier. These streams are brought together in a small jet mixer which minimizes the total volume of proplnt. Upon leaving the mixer, the carrier is largely separated from the proplnt by gravity. The remaining mixt is vacuum cast which removes the remaining carrier.

B. Cost Trade-Offs
All rocket motor costs per unit, and therefore rocket proplnt costs, are most sensitive to the number of units being produced and to the number of different formulations mixed in a given time interval, by the same equipment, so that a direct comparison based only on processes or proplnt types are meaningless. There are also inherent difficulties in comparing NC base proplnts with composite proplnts. The former are made in government plants (some of which are operated by private industry) for the most part and so accounting for indirect costs (taxes, depreciation, insurance, and return on investment) cannot be compared to the situation.
Table 25
Mixer Production Cost Comparison for Composite Propellants *

<table>
<thead>
<tr>
<th></th>
<th>1 million lbs/month</th>
<th>3 million lbs/month</th>
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<td>With materials**</td>
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<tr>
<td>Continuous mix — direct cast</td>
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<td>$0.79</td>
</tr>
<tr>
<td>Continuous mix — transport to cast</td>
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<td>0.81</td>
</tr>
<tr>
<td>300-gallon vertical batch</td>
<td>0.33</td>
<td>0.84</td>
</tr>
<tr>
<td>150-gallon vertical batch</td>
<td>0.46</td>
<td>1.00</td>
</tr>
<tr>
<td>Continuous mix — transport to cast (processing 3 dissimilar formulations per week)</td>
<td>0.32</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* 1964 data
** material cost @ $0.40 per lb

where private industry owns the plants making composite propellants. Another factor making comparison impossible is the fact that most double-base propellants go into the smaller rockets, whereas composites are best suited to the larger rockets and space boosters.

It is possible to make a somewhat meaningful comparison of mixer costs for composite propellants made in large volume production in the various large mixers. McGeehe (Ref 42) did so using 1964 prices and the data are summarized in Table 25. He concluded that continuous mixing produced composite propellants at less cost/lb than any of the known vertical mixers at the time (when processing a single formulation at rates of 1 million pounds per month and up). However, when three dissimilar formulations per week were required, the total propellant production cost per pound became cheaper for the 300-gallon vertical mixer. At 2 million pounds per month the costs were roughly equal. The major reasons for this are that the propellant losses become significant and maintenance costs increase for the continuous mixer on turnarounds. Since most contractors produce a variety of formulations, most propellant is made in large vertical mixers.

V. Physical Characteristics of Representative Propellants
   A. Mechanical Properties
   NC content is a major compositional variable affecting the physical properties of tensile strength, elongation, and modulus of elasticity of cast double-base propellants. Steinberger (Ref 21) has reported the data shown in Figs 2, 3 & 4 for temps ranging from −60° to 120°F.

McAbee (Ref 31) measured the tensile properties of two cast double-base rocket propellants (OGK and ARP) and two extruded materials (T-16 and X-8) at 25° over a range of loading times from 0.005 to 2500 seconds. The effects of temp were also investigated at 0.1 inch/inch/min (conventional static test rate) and at high rates of loading over a range of −60° to 80°. Typical curves showing the stress-strain behavior of X-8 and OGK over the temp range are given in Figs 5 & 6 for the nominal strain rate of 0.1 inch/inch/min. Variable loading rates produce the type of stress-strain behavior indicated in Fig 7 for X-8 at 25°.

Since these double-base propellants consist essentially of a single phase which bears the total load in any application of force, their mechanical property behavior is significantly different from composite propellants. In the latter formulations, the hydrocarbon binder comprises only about 14% of the composite structure, the remainder being solid particles. Under stress, the binder of these propellants bears a proportionately higher load than that in the single phase double-base propellants. At small strain levels, these propellants behave in a linear viscoelastic manner where the solids reinforce the binder. As strain increases, the bond between the oxidizer and binder breaks down.
Fig 2  Tensile strength of cast double-base powder as a function of nitrocellulose content

Fig 3  Elongation of cast double-base powder as a function of nitrocellulose content

Fig 4  Modulus of elasticity of cast double-base powder as a function of nitrocellulose content
Fig 5  Effect of temperature on the stress-strain behavior of X-8 at 0.1 inch/inch/min

Fig 6  Effect of temperature on the stress-strain behavior of OGK at 0.1 inch/inch/min
Reliable data in the literature for the stress versus strain properties of composite propellants are exceedingly difficult to find. Since the binder chemical properties and curing additions are susceptible in many cases to hydrolytic degradation, the exact formulations under test should be specified. Additionally, the binder to oxidizer adhesion properties are dependent upon particle size distribution used in the propellant. This should be specified and in almost all literature sources unearthed, it remained unknown. As some of these data show, the manner of conducting the test and control of such ambient conditions as relative humidity also influences the result. Consequently, the data presented herein should be used only to estimate the effects that certain binder types and sample processing conditions can produce on the mechanical properties reported.

Some typical stress-strain curves for a carboxy-terminated polybutadiene propellant (CTPB) containing 86% solids are given in Figure 8, and for a PBAA propellant (see Table 13) containing 83% solids in Figure 9 (Ref 52). The authors concluded that the CTPB propellants studied were highly susceptible to humidity degradation.
Fig 8  Effect of Storage Condition Upon the Mechanical Properties of CTPB#2 Propellant

Fig 9  Effect of Aging (70°) and Average Humidity During Processing/Testing Upon the Mechanical Properties of PBAA (83% Solids) Propellant
Fig 10  Ambient Temperature Aging of Polybutadiene Propellants

Fig 11  160°F Aging of Polybutadiene Propellants
The influence of ambient aging at 70°F and accelerated aging at 160°F on the stress-strain behavior of carboxy-terminated polybutadiene, polybutadiene-acrylic acid, polybutadiene-acrylic acid-acrylonitrile, and hydroxy-terminated polybutadiene composite propellants is shown in Figures 10 and 11. The elastomers and curative agents for these formulations are listed below:

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<th>Formulation</th>
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<td>MAPO/PMAPO</td>
</tr>
<tr>
<td>LPC-544A*</td>
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<td>CT PB</td>
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</table>

*Contains ferrocene

Whether any of the formulation variables change the mechanical properties significantly upon aging cannot be answered due to the lack of definition of chemical composition parameters as discussed previously.

For the reader interested in more elaborate treatments of the influence of mechanical properties upon rocket motor service life, the meeting papers of the Interagency Chemical Rocket Propulsion Group, Mechanical Behavior Working Group, as published by the Chemical Propulsion Information Agency are recommended.

Under increasing strain the propellant volume increases from the voids created around the unbonded solid particles. Nonlinearities in Young’s modulus and Poisson’s ratio then occur. Francis (Ref 50) shows this effect for a carboxy-terminated polybutadiene composite propellant with 14% binder as in Figure 12. He concludes that nonlinearities in low-temperature properties reduce the predicted stress and strain values upon cooling a solid motor, and therefore a structural analysis that neglects these effects will be conservative. However, when the predictions are extended to a pressurized fiberglass motor case, the nonlinearities in properties produce greater strains than those predicted with linear analysis.

Prediction of the service life of the solid propellant third-stage Minuteman motor has been made by Chappell (Ref 48). This motor has a fiberglass case and a cast double-base grain. The motor parameters on which the structural safety margin depends are: (1) motor geometry, (2) case thickness (elastic tensile modulus and Poisson’s ratio), (3) propellant stiffness (tensile relaxation modulus and bulk modulus), (4) propellant strength (strain at maximum stress versus strain rate), and (5) ignition pressure transient.

Both stress relaxation modulus and strain at maximum stress were determined from samples from aged (7 years) operational motors that were sectioned and sampled for that purpose. These data are presented in Figures 13 and 14. The service life (10 years) was estimated by using a cumulative damage approach similar to Mina’s rule for fatigue in metals (Ref 37).
B. Chemical Factors Contributing to Aging

Many propellant systems have built-in defects which contribute to degradation of the polymer system and reduce service life. The polyurethane binder systems react adversely to water. As a result, the ingredients must be dried thoroughly before processing. The following reaction illustrates the sequence that occurs between a monofunctional isocyanate and water:

\[
R-\text{N}=\text{C}=\text{O} + \text{HOH} \rightarrow \text{RNH}_2 -\text{C}=\text{OH} \quad (0) \\
\text{RNH}_2 -\text{C}=\text{OH} \rightarrow \text{RNH}_2 + \text{CO}_2 \\
\text{RNH}_2 + R-\text{N}=\text{C}=\text{O} \rightarrow \text{R-NH}_2 -\text{C}=\text{NH}_2 \\
\]

In this way one mole of water reacts with two moles of isocyanate. For a urethane prepolymer with an equivalent weight of about 300, it only takes 9 grams of water to effectively consume the prepolymer. This can lead not only to degraded physical properties, but it also forms gas bubbles in the propellant which lead to voids and higher than predicted burning rates. This sensitivity to water content also exists with hydroxymethylated polybutadiene polymers cured with
isocyanates. In contrast, carboxy-terminated polybutadiene polymers are relatively insensitive to water content when cured with epoxies.

Some binder systems have used MAPO as the only curing system for carboxy-terminated polybutadiene polymers. Again a problem in long-term stability of physical properties is sometimes encountered since MAPO is hydrolytically unstable. The following reaction is possible:

\[
\text{O-P} \left( \begin{array}{c}
\text{N} \\
\text{CH}_2 \\
\text{CH}_3
\end{array} \right)_3 + 3\text{OH} \rightarrow \text{O-P} \left( \begin{array}{c}
\text{CH}_3 \\
\text{N-CH}_2\text{CH}_2
\end{array} \right)_3 \text{H}
\]

and a slow degradation of physical properties with time may occur. Again, drying of all propellant ingredients is of importance.

The composite propellants are not the only ones subject to degradation processes which affect shelf-life, although they are relative newcomers to propellant history. In NC-based propellants, NC decomposes slowly to release NO\(_2\) which reacts catalytically to hasten the degradation in physical and ballistics properties. To slow the process, stabilizing agents such as diphenylamine or 2-nitrodiphenylamine are added to react with the NO\(_2\). The first reaction product is diphenylnitrosamine, followed by ring nitration. When the stabilizer is used up, for all purposes the shelf-life of the propellant is ended.

VI. Chemical Characteristics and Performance

A. Burning Rate

For the conventional treatment of both double-base and composite propellant burning rates, the reader is referred to Refs 22, 33 & 51. This article will review recent papers and patent literature which disclose new advances in the state-of-the-art. In the past, the burning rates of double-base propellants have been modified by using such lead salts as lead salicylate, lead acetyl salicylate, lead azide, lead stearate, lead oxide, lead 2-ethyl hexoate, and others. There are several objectives in using these salts. One is to produce a plateau or mesa effect where the burning rate of the plateau propellant remains relatively constant over a stated pressure range and the burning rate of the mesa propellant decreases with pressure over stated ranges. Lantz (Ref 81) recently found that thorium salts such as the malonate, malate, tartrate, cyclopentane carboxylate, stearate, salicylate, resorcylate, succinate, pimelate, adipate, and mixtures thereof impart mesa and plateau characteristics in double-base propellants. Examples of propellant compns employing this ballistic modifier are shown in Table 26, and representative burning rate curves from \(-40^\circ\) to \(160^\circ\) are shown in Figure 15.

Although the specific impulse of double-base propellants can be substantially increased by incorporating aluminum and AP in conventional formulations, they become highly temp sensitive with relatively high pressure exponents (n). Propellants with exponents much above 0.5 are subject to undesirably high fluctuations in performance induced by small changes in combustion pressure. Shaver (Ref 64) found that decreases in temp sensitivity and pressure exponents of such formulations can be achieved by using fine particle aluminum along with variations in the particle size of the AP used. It was also found that an organic lead salt could be used with these formulations to increase the burning rate, a catalytic phenomenon not encountered with the conventional aluminized double-base propellant. The effects of the stated compositional changes on temp and pressure sensitivities are shown in Tables 27 and 28.

Recent technology advances in both offensive and defensive missiles have generated a requirement for high burning rate propellants to achieve high acceleration rates and reduced time to target. In double-base propellants, high burning rates have been achieved with derivatives of carborane and biradical burning rate catalysts. Hill (Ref 68) described the use of 1,1-isopropenyl-1,2-prop-(2-one)-yl-carborane (IPCA),

\[
\text{H}_2\text{C} = \text{C} - \text{C} - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_3
\]

in aluminized double-base formulations plasticized with TEGDN. His data in Table 29 compare burning rates for 12% IPCA to a control without this ballistic modifier. Most carborane derivatives are not compatible with NC; so this compound is an exception. Further increases in burning rate may be achieved by using ultrafine AP. The rate at 2000psi for the composition containing IPCA shown in Table 29 is increased to 6.5 inches/sec by substituting 2.5 micron particle size AP for the 8 and 15 micron blend shown.
<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (%)</th>
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</tr>
</thead>
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<td>Carbon Black</td>
<td>32</td>
<td>Black Oxide</td>
<td>10</td>
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<tr>
<td>Carbon Black</td>
<td>33</td>
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<td>40</td>
<td>Black Oxide</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 26**

Additional Examples
Sales (Ref 80) used the biradical compounds, p,p'-biphenylene-bis(diphenylmethyl),

\[(C_6H_5)_2C \stackrel{\mathcal{C}}{\longrightarrow} C(C_6H_5)_2,\]

and p,p'-phenylene-bis(diphenylmethyl),

\[(C_6H_5)_2C \stackrel{\mathcal{C}}{\longrightarrow} C(C_6H_5)_2,\]

as high burning rate catalysts for crosslinkable double-base propellants. The burning rates of propellant composites with this biradical catalyst are compared in Table 30 to a conventional double-base with lead peroxide as a burning rate catalyst. Not only do these composites promote burning rates, but they also function as inhibitors for resonance burning and combustion instability. It is not known whether these will function as catalysts for aluminized double-base formulations as most of the lead salts do not when aluminum is introduced.

In contrast to the difficult problem of accelerating the burning rates of double-base propellants, the options open to the composite propellant formulator are many. These may be grouped under the categories of carborane derivatives, carborane plus NF derivatives, metal staples, fine particle ammonium perchlorate, ferrocene derivatives, free radical and biradical composites. As demands for higher burning rates are pressed, it should be remembered that at the higher burning rates the combustion control problems and rocket motor design problems become greater. The transition point between deflagration and detonation becomes more blurred. There is also a decided trend to inherit physical and chemical stability problems along with the enhanced burning rates.

The burning rates of standard aluminized hydrocarbon binder composite propellants may be increased significantly not only with ferrocene derivatives but also with compatible carborane-type burning rate additives. However, most ferrocene derivatives are volatile solids or liquids which have a tendency to evaporate from the propellant during storage, thereby degrading ballistic performance. Rudy (Ref 71) minimized this problem by the use of polynuclear ferrocene...
Table 27

<table>
<thead>
<tr>
<th>Formulation</th>
<th>BR in/sec</th>
<th>$\sigma_p$</th>
<th>$\pi_{kn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.44</td>
<td>0.62</td>
<td>0.21</td>
</tr>
<tr>
<td>B</td>
<td>0.32</td>
<td>0.64</td>
<td>0.19</td>
</tr>
<tr>
<td>C</td>
<td>0.46</td>
<td>0.47</td>
<td>0.13</td>
</tr>
<tr>
<td>D</td>
<td>0.38</td>
<td>0.48</td>
<td>0.10</td>
</tr>
</tbody>
</table>

1 The value of the pressure exponent was the same at each of the three test temps, -20°F, 70°F and 165°F
2 $\pi_{kn} = \sigma_p/(1-n)$
3 Temp coefficient of burning rate at constant pressure, $\sigma_p = (\partial \ln BR / \partial T)_p$

Sample A
- NH$_4$ClO$_4$ D$_W$ 25 microns 13.39
- NH$_4$ClO$_4$ D$_W$ 200 microns 13.39
- Al D$_W$ 18 microns 23.22

Sample B
- NH$_4$ClO$_4$ D$_W$ 200 microns 26.78
- Al D$_W$ 18 microns 23.22

Sample C
- NH$_4$ClO$_4$ D$_W$ 200 microns 26.78
- Al D$_W$ 1 micron 23.22

Sample D
- NH$_4$ClO$_4$ D$_W$ 200 microns 26.78
- Al D$_W$ 300 A 10.00
- Al D$_W$ 18 microns 13.22

Table 28

<table>
<thead>
<tr>
<th>Formulation</th>
<th>BR in/sec at 70°F</th>
<th>$\sigma_p$</th>
<th>$\pi_{kn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0.43</td>
<td>0.52</td>
<td>0.21</td>
</tr>
<tr>
<td>F</td>
<td>0.52</td>
<td>0.37</td>
<td>0.13</td>
</tr>
<tr>
<td>G</td>
<td>0.46</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>

Propellant grains were prepared according to the oxidizer grind of Example 1, as follows:

Sample E
- Same as Sample A, Example 1, plus 2.00 parts by weight of lead salicylate

Sample F
- Same as Sample C, Example 1, plus 2.00 parts by weight of lead salicylate

Sample G
- Same as Sample D, Example 1, plus 2.00 parts by weight of lead salicylate

Table 29

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC, D$_W$ 15 microns</td>
<td>21.50</td>
</tr>
<tr>
<td>2-Nitrodiphenylamine</td>
<td>1.00</td>
</tr>
<tr>
<td>(2NDPA - stabilizer)</td>
<td></td>
</tr>
<tr>
<td>NG/dibutyl phthalate, 3:1</td>
<td>25.02</td>
</tr>
<tr>
<td>Dibutyl sebacate</td>
<td>2.48</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>26.78</td>
</tr>
<tr>
<td>Aluminum</td>
<td>23.22</td>
</tr>
</tbody>
</table>

Component:
- Nitrocellulose: 12.0
- TEGDN: 35.0
- Aluminum: 2.0
- Ammonium perchlorate:
  - 8 micron: 40.0
  - 15 micron: 8.0
- Adiponitrile: 3.0
- IPCA: 12.0
- Resorcinol: 1.0

Burning rate (inches/sec):
- 2,000psi: 2.00
- 1,000psi: 1.30
- 500psi: 0.83
Table 30
A Comparison of Crossinkable Double-Base Propellants With and Without Burning Rate Catalyst

<table>
<thead>
<tr>
<th>Ingredients/Burning Rate</th>
<th>Propellant Compositions Percent by Weight and Burning Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Casting Powder* (binder)</td>
<td>11.25</td>
</tr>
<tr>
<td>Triethylene Glycol Dinitrate (TEGDN)</td>
<td>28.75</td>
</tr>
<tr>
<td>Butanetriol Trinitrate (BTNN)</td>
<td>15.5</td>
</tr>
<tr>
<td>Cyclotetramethylenetetranitramine (HMX)</td>
<td>40.0</td>
</tr>
<tr>
<td>Lead Peroxide</td>
<td></td>
</tr>
<tr>
<td>p,p'-Biphenylene-bis(diphenylmethyl)</td>
<td></td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.5</td>
</tr>
<tr>
<td>Toluene Disocyanate (added)</td>
<td>1.0</td>
</tr>
<tr>
<td>Burning Rate (ips at 1000psia)</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*Casting powder formulation:
10.1 parts nitrocellulose
 .95 parts nitroglycerine
 .20 parts 2-nitrodiphenylamine

TOTAL 11.25 parts Casting powder

derivatives which have low vapor pressures and do not tend to evaporate or migrate from the propellant. The compounds are prep by reacting a hydroxymethylene-substituted ferrocene such as n-butyl ferrocene with an aliphatic aldehyde such as methylal in diethyl ether. The following general structural formula appears to represent the products which are mixts of combs of varying molecular weight and isomerism:

\[(RR'\text{C}_{10}H_6Fe)CH\]

\[\text{[(RR'\text{C}_{10}H_6Fe)CH] (RR'R'\text{C}_{10}H_6Fe)}\]

The crude product from the above reaction mixt was fractionated into a distilled product (bp 200°/0.3 Torr) with an average molecular weight of 514 and a residue with an average molecular weight of 940. These were evaluated as catalysts and compared to prior art ferrocenes in a standard carboxy-terminated polybutadiene formula cured with MAPO. The results are shown in Table 31.

Table 31

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration % Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxy-terminated polybutadiene</td>
<td>11.35</td>
</tr>
<tr>
<td>Thiokol HC-434</td>
<td>0.65</td>
</tr>
<tr>
<td>Tris[1-(2-methyl) aziridinyl] phosphine oxide (MAPO)</td>
<td></td>
</tr>
<tr>
<td>Dioctyl adipate + combustion catalyst</td>
<td>5.00</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>83.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Burning Rate at 1000psia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Conc. %w</td>
</tr>
<tr>
<td>None</td>
<td>0.36</td>
</tr>
<tr>
<td>Crude</td>
<td>1.0</td>
</tr>
<tr>
<td>Distillate</td>
<td>1.0</td>
</tr>
<tr>
<td>Distillate</td>
<td>3.0</td>
</tr>
<tr>
<td>Residue</td>
<td>1.0</td>
</tr>
<tr>
<td>Residue</td>
<td>3.0</td>
</tr>
<tr>
<td>Ferrocene</td>
<td>1.0</td>
</tr>
<tr>
<td>Ferrocene</td>
<td>3.0</td>
</tr>
<tr>
<td>n-Butylferrocene</td>
<td>1.0</td>
</tr>
<tr>
<td>n-Butylferrocene</td>
<td>3.0</td>
</tr>
<tr>
<td>Dimethylferrocene</td>
<td>1.0</td>
</tr>
<tr>
<td>Dimethylferrocene</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Table 32

<table>
<thead>
<tr>
<th>Ingredient, wt percent:</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td>68.0</td>
<td>68.0</td>
<td>68.0</td>
</tr>
<tr>
<td>Aluminum</td>
<td>14.0</td>
<td>14.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Carboxyl-terminated polybutadiene prepolymer</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
</tr>
<tr>
<td>n-Butylferrocene</td>
<td>7.0</td>
<td>7.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Tris(methylaziridinyl)-phosphine oxide</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Tris(oxyaryl)-para-aminophenol</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron linolate</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Leithin</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>1,2-bis(2,3-epoxypropyl) carborane</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1-(2,3-epoxypropyl) carborane</td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Burning rate (1000 psi) inches/sec</td>
<td>1.2</td>
<td>1.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 33

<table>
<thead>
<tr>
<th>Composition</th>
<th>Per Cent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butarez CTL (Carboxy-terminated polybutadiene polymer)</td>
<td>8.28 8.28 8.28</td>
</tr>
<tr>
<td>MAPO(^1)</td>
<td>0.31 0.31 0.31</td>
</tr>
<tr>
<td>IDP(^2)</td>
<td>5.41 5.41 5.41</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>64.00 64.00 64.00</td>
</tr>
<tr>
<td>Copper Chromite</td>
<td>1.00 1.00 1.00</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>21.00 19.00 17.00</td>
</tr>
<tr>
<td>Aluminum staple(^3)</td>
<td>2.00 4.00</td>
</tr>
<tr>
<td>Burning rate (1000 psi, 70°F)</td>
<td>0.53 0.71 1.00</td>
</tr>
<tr>
<td>Specific impulse (lb-sec/lb)</td>
<td>232.30 229.20 233.40</td>
</tr>
</tbody>
</table>

\(^1\) tris[1-(2-methyl) aziridinyl] phosphine oxide  
\(^2\) isodecylpelargonate  
\(^3\) size of staple .125” x .0025” x .0005”

Sayles (Ref 67) combined n-butylferrocene with 1-(2,3-epoxyaliphatic) carboranes of at least 3 carbonations in the aliphatic chain to function both as burning rate catalysts and cross-linking agents for carboxylated polybutadiene and acrylate binders. The use of 1,2-bis(2,3-epoxypropyl) carborane and 1-(2,3-epoxypropyl) carborane boosted the burning rate of a butylferrocene propellant from 1.2 to 1.9 inches/sec as the data in Table 32 indicates.

The use of ultra-fine AP to increase the burning rates of double-base propellants has been described previously. This technology has also been used with hydrocarbon binders, but dispersion and high viscosity have presented mixing problems. Fine AP can be conveniently dispersed by slurrying first with a surfactant and an organic liq such as 1,1,2-trichloro-1,2,2-trifluoroethane or normal hexane in a process described by Alley (Ref 58a). Sodium sulfonate
Table 34
A Comparison of a Carboxyl-Terminated Polybutadiene-Based Propellant (CTPB)
Using N-Butylferroocene as Burning Rate Catalyst With a CTPB-Based Propellant
Using Biradical Burning Rate Catalyst

<table>
<thead>
<tr>
<th>Propellant Ingredients/Burning Rate</th>
<th>Propellant Composition Percent by Weight/Burning Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Ammonium Perchlorate</td>
<td>66</td>
</tr>
<tr>
<td>Aluminum</td>
<td>14</td>
</tr>
<tr>
<td>Normal-Butylferroocene</td>
<td>7</td>
</tr>
<tr>
<td>p,p'-Biphenylene-bis(diphenylmethyl)</td>
<td>-</td>
</tr>
<tr>
<td>Carboxylic Terminated Polybutadiene</td>
<td>12.5</td>
</tr>
<tr>
<td>Tris[1-(2-methyl)aziridinyl] phosphine oxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Tris(oxiranyl)-para-aminophenol (added)</td>
<td>0.1</td>
</tr>
<tr>
<td>Iron Linoleate (added)</td>
<td>0.1</td>
</tr>
<tr>
<td>Burning Rate (ips at 1000 psi)</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 35
Burning Rate Data on Butadiene-CMA Copolymers in Propellant Formulations

<table>
<thead>
<tr>
<th>Copolymer No</th>
<th>Boron Content (% of propellant)</th>
<th>Burning Rate (in/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>800–824 psi</td>
</tr>
<tr>
<td>Standard</td>
<td>0</td>
<td>0.501</td>
</tr>
<tr>
<td>6</td>
<td>0.20</td>
<td>0.529</td>
</tr>
<tr>
<td>7</td>
<td>0.42</td>
<td>0.542</td>
</tr>
<tr>
<td>8</td>
<td>0.78</td>
<td>0.558</td>
</tr>
<tr>
<td>9</td>
<td>0.81</td>
<td>0.660</td>
</tr>
</tbody>
</table>

Butadiene/CMA copolymer binder — 10.0 wt %
Isodecyl Pelargonate plasticizer — 10.0
Aluminum Powder — 10.0
Ammonium Perchlorate (5.6%) — 70.0

Physical Property Data on Butadiene-CMA Copolymers

<table>
<thead>
<tr>
<th>No</th>
<th>Molecular Weight</th>
<th>Weight % OH Calc'd*/Found</th>
<th>% B in Polymer Calc'd**/Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3200</td>
<td>1.06</td>
<td>2.32</td>
</tr>
<tr>
<td>7</td>
<td>3300</td>
<td>1.03</td>
<td>4.69</td>
</tr>
<tr>
<td>8</td>
<td>3600</td>
<td>0.94</td>
<td>4.02</td>
</tr>
<tr>
<td>9</td>
<td>2600</td>
<td>1.31</td>
<td>10.07</td>
</tr>
</tbody>
</table>

* Calculated OH content is based on observed molecular weight, with the assumption that each molecule contains two hydroxyl groups
** Based on monomer charge
in mineral oil was found to be a satisfactory surfactant at the 0.1 to 0.5 weight percent level. After the AP is dispersed, the binder is mixed in and the organic liq removed by evaporation.

The burning rates of carboxy-terminated polybutadiene composite propants have been approximately doubled by using metal staples made from aluminum and other metals such as silver or copper according to Madden (Ref 83) and Lawrence (Ref 66). Data for a carboxy-terminated polybutadiene are given in Table 33 (Ref 83). The embedded staples are effective regardless of the specific compn of the proplnt, although the actual increase in ballistic performance and burning rate will vary to some extent according to the specific proplnt compn. Increased staple content along with burning rate catalysts have given burning rates at 1000 psi up to 3.9 inches/sec (Ref 66).

The biradical catalysts described previously for double-base propiants (Ref 80) are also effective for hydrocarbon propiants. Table 34 shows how p,p'-biphenylene-bis(diphenylmethyl) compares to n-butyl ferrocene as a catalyst in a carboxy-terminated polybutadiene. These catalysts are claimed to overcome all of the processing difficulties, chemical stability and volatility disadvantages attributed to catalysts based on ferrocene and carborane derivatives. Another somewhat similar functioning catalyst, the free radical compd, 2,2-diphenylpicrylhydrazyl, is far less effective as a burning rate catalyst (Ref 54).

Another approach to high burning rate propiants has been to incorporate an energetic compd based on a carborane derivative into the polymer. Both copolymers and terpolymers have been prepared based upon carboranymethacrylate (CMA). Typically, butadiene is reacted with carboranymethacrylate to give a copolymer with a molecular weight of 3500, a hydroxy end group content of 0.6 and boron equal to 13.5 weight percent. Baldwin (Ref 65) formulated the polymers described in Table 35 into composite propiants which gave a 30% increase in burning rate over the standard proplnt without the copolymer.

Baldwin (Ref 65) also synthesized a copolymer from acrylic acid and carboranymethacrylate which was used to make the propiants in Table 36. Composition A has the burning rates shown in the table for the AP particle sizes indicated. Composition B had an average AP particle size of 15 microns and a burning rate of 1.75 millimeters/sec.

**Table 36**

<table>
<thead>
<tr>
<th>Particle Size (Normal)</th>
<th>Burning Rate, in/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 micron</td>
<td>2.0</td>
</tr>
<tr>
<td>45 micron</td>
<td>2.2</td>
</tr>
<tr>
<td>35 micron</td>
<td>2.4</td>
</tr>
<tr>
<td>15 micron</td>
<td>3.0</td>
</tr>
<tr>
<td>5 micron</td>
<td>3.6</td>
</tr>
</tbody>
</table>

**Composition A**

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td>55.0</td>
</tr>
<tr>
<td>Aluminum (powder)</td>
<td>5.0</td>
</tr>
<tr>
<td>Carboranymethacrylate/</td>
<td>22.06</td>
</tr>
<tr>
<td>Acrylic acid (95/5) prepolymer</td>
<td></td>
</tr>
<tr>
<td>Triethyleneglycol dinitrate</td>
<td>14.70</td>
</tr>
<tr>
<td>Dicyclo diepoxy carboxylate (UNOX 221)</td>
<td>3.09</td>
</tr>
<tr>
<td>Ferric acetylaconate</td>
<td>0.15</td>
</tr>
<tr>
<td>(curing agent, catalyst)</td>
<td></td>
</tr>
</tbody>
</table>

**Composition B**

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate (5 μ)</td>
<td>42.0</td>
</tr>
<tr>
<td>Ammonium perchlorate (45 μ)</td>
<td>14.0</td>
</tr>
<tr>
<td>Aluminum (powder)</td>
<td>5.0</td>
</tr>
<tr>
<td>Carboranymethacrylate/</td>
<td>16.3</td>
</tr>
<tr>
<td>Acrylic acid (95/5) prepolymer</td>
<td></td>
</tr>
<tr>
<td>Triethyleneglycol dinitrate</td>
<td>10.8</td>
</tr>
<tr>
<td>Butanetriol trinitrate* (contains in</td>
<td>10.9</td>
</tr>
<tr>
<td>addition 2 parts of dicyclo diepoxy</td>
<td></td>
</tr>
<tr>
<td>carboxylate per 100 parts of propiant)</td>
<td></td>
</tr>
</tbody>
</table>

*Also known as 1,2,4-trinitrobutane

Dicyclo diepoxy carboxylate is a curing agent. A dicyclo diepoxy carboxylate curing agent is sold under Union Carbide Corporation’s trademark UNOX 221.
rate of 3.65 inches/sec at 2000psi. No data were given for the pressure exponents which in many carborane derivative propellants are well above 0.5.

Terpolymers of butadiene, carboranymeth-acrylate (CMA) and acrylic acid have been used to formulate propellants with high burning rates by Huskins (Ref 78). The comps of these propellants are given in Table 37. Burning rates at 1000psi ranged from 0.25 inch/sec for the standard, to 0.4 inch/sec for 25% CMA in the terpolymer and to 3.5 inches/sec for 75% CMA in the terpolymer. It was found that burning rate was proportional to CMA content. These terpolymers were also combined with polybutadiene-acrylic acid copolymer and carboxy-terminated polybutadiene polymers with similar increases in burning rates.

A final class of high burning rate propellants combines the high density and high impulse difluoramino comps in their binders with the carborane derivatives. Jones (Ref 79) described the preparation of TVOPA (1,2,3-tris[1,2-bis[(difluoramino)ethoxy] propane, IPCA (1-isopropenyl-carboranyl-acetone) and NFPA (2,3-bis(difluoramino) propyl acrylate) and propellants.

| Table 37 |
|----------|--------|--------|
| Compn    | Ingredients                        | Percent by Weight |
| A        | Terpolymer (25% CMA)               | 19.7              |
|          | AP                                | 64.0              |
|          | Aluminum powder fuel               | 16.0              |
|          | Lecithin                          | 0.3               |
|          |                                   | 100.0             |
| B        | Terpolymer (50% CMA)               | 19.7              |
|          | AP                                | 64.0              |
|          | Aluminum powder fuel               | 16.0              |
|          | Lecithin                          | 0.3               |
|          |                                   | 100.0             |
| C        | Terpolymer (75% CMA)               | 19.7              |
|          | AP                                | 64.0              |
|          | Aluminum powder fuel               | 16.0              |
|          | Lecithin                          | 0.3               |
|          |                                   | 100.0             |
| D        | Carboxy-terminated poly-butadiene  | 19.7              |
| (standard)|                                  | 64.0              |
|          | AP                                | 16.0              |
|          | Lecithin                          | 0.3               |
|          |                                   | 100.0             |

<table>
<thead>
<tr>
<th>Table 38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burning Rates, Densities, and Specific Impulses for Ethyl Acrylate Propellants Containing TVOPA Modifier</td>
</tr>
<tr>
<td>Component</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>EA</td>
</tr>
<tr>
<td>AA</td>
</tr>
<tr>
<td>TVOPA</td>
</tr>
<tr>
<td>IPCA</td>
</tr>
<tr>
<td>AP (8 micron)</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Additive: UNOX 221</td>
</tr>
<tr>
<td>(dicyclo dieoxy carboxylate curing agent)</td>
</tr>
<tr>
<td>Density (lbm/in³)</td>
</tr>
<tr>
<td>&quot;sps (lbf-sec/lbm)</td>
</tr>
<tr>
<td>Burning Rate (in/sec)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

a Calculated impulse, 1000psi chamber pressure, standard condition
containing these ingredients. His data for typical formulations are given in Tables 38 and 39. EA refers to ethyl acrylate and AA to acrylic acid. There are a number of problems with such propellants. The pressure exponent, \( n \), of 0.88 signifies extreme problems in achieving stable burning in practical rocket motors. Other disadvantages include marginal safety characteristics of sensitivity to shock, chemical stability in contact with AP, and the high cost of raw materials.

B. Ignition theories

Price (Ref 39) compares the three principal quantitative models of ignition and concludes that there are serious deficiencies in the existing models, so much so that no one theory appears adequate to represent the complexity of ignition of composite solid propellants. In the gas-phase model (Refs 22 & 36) the hot oxidizing environment gas and fuel vapors from the propellant mix and react to provide a self-sustaining heat source. The heterogeneous ignition theory (Ref 30) assumes that the sole source of heat is a heterogeneous surface reaction between powerful oxidizing gases given off by the decomp of AP and fuel binder constituents. The hypergolic ignition theory (Refs 26 & 29) evolved from the study of the ignitability of binders and propellants by CIF\(_3\) and F\(_2\). In the limiting case where the solid oxidizer is the sole source of oxidizing species, the theory becomes the same as the heterogeneous ignition theory. The ignition theories for NC base propellants differ from composite propellants because of the inclusion of oxygen in the reactive sequences envisioned. Summerfield proposes a gas-phase ignition mechanism for double-base propellants with the oxygen content of the igniting gas having an active role in ignition (Ref 25). The importance
of runaway reactions in the solid phase has also been emphasized (Ref 56). Hicks (Ref 18) proposed the solid phase thermal theory of ignition which led to a transient surface heating analysis with exothermic chemical heating in the solid with an exponential dependency of rate on temp. This model was compatible with the known exothermic decomp of propints of the NC-NG type. Upon introduction of composite propints, the need for a different mechanism became apparent.

The varied and conflicting ignition theories can be reconciled if one appreciates the fact that more than one possible mechanism of ignition probably exists and the varying experiments designed to prove the theories accentuate the particular mechanism discussed. Generally the experimentalists have developed data which strongly supports the heterogeneous ignition theory for composites containing AP. The initial low-temp step is the proton transfer which results in the formation of absorbed NH₃ and HClO₄. Further decomp of HClO₄ yields ClO₃ and ClO₄ followed by the rapid decomp of the unstable chloride oxides to yield O atoms and ClO radicals, which oxidize NH₃ and react heterogeneously with solid fuel. The experiments of Fishman (Ref 46) disclosed a surface exotherm preceding ignition at high heat fluxes which is clearly associated with surface reactions, the heterogeneous decomp of HClO₄ and subsequent oxidation of the fuel. In support of this theory, the experiments of Pearson (Refs 38 & 44) showed that ignition occurred when either oxygen at about 400° or perchloric acid at 200–300° contacted solid propint fuels. With NH₃, ignition was achieved only on copper chromate catalyst via a heterogeneous reaction.

C. Specific Impulse

As developed from the equation for conservation of momentum (Ref 27), the thrust, F, on a rocket motor is

\[
F = (\frac{1}{2} + \frac{1}{4} \cos \alpha) (\dot{W} V_e / g) + (P_e - P_0) A_e
\]

where \( \alpha \) = half of the divergence angle of the nozzle, \( \dot{W} \) = weight rate of propint flow, \( g \) = acceleration of gravity, \( V_e \) = exit flow velocity, \( P_e \) = nozzle exit pressure, \( P_0 \) = external atm pressure, and \( A_e \) = cross section at nozzle exit plane. An effective exhaust velocity is defined by

\[
C = (\frac{1}{2} + \frac{1}{4} \cos \alpha) V_e + \frac{(P_e - P_0) A_e}{\dot{W} / g}
\]

and the thrust becomes,

\[
F = \dot{W} C / g
\]

Maximum thrust is attained when \( P_e = P_0 \) and \( \alpha \) is made small, then

\[
C = V_e \quad \text{and} \quad F = \dot{W} C / g = \dot{W} V_e / g
\]

The specific impulse is the thrust per unit weight rate of flow and so,

\[
I_{sp} = F / \dot{W} = C / g
\]

Experimentally thrust is measured by standard procedures (Ref 33) which put rigid specifications on motor sizes, test equipment and data reduction. Prior to obtaining exptl proof of performance by expensive test procedures, most prudent investigators will make theoretical calcns of the specific impulse as a measure of propint performance since this parameter is basically a property of propint compn. A theoretical value for \( I_{sp} \) is calc by consideration of the thermochemistry of the chemical reaction in the rocket combustion chamber and in the expansion process. The basic development of the mathematical equations used in this type of calcn is given in Ref 27. The calcn is sufficiently complicated in the case of multi-component systems so that the use of digital computers is required to reduce the time required for the estimation. Such programs and services are available to government agencies and contractors for nominal fees (Refs 49 & 60). Tables 40–48 list physical and thermochemical properties required for performance calcns for the most common fuels and oxidizers used in solid propints (Ref 43).

The influence of \( \text{CH}_2 \text{CHOH} \) binder content on the theoretical specific impulse of AP composite containing 8, 12 and 16% aluminum reaches a max at binder contents between 10 and 15% as shown in Fig 16, while the max level of acceptable physical properties occurs at the 10–16% level. Most operational propints accept a sacrifice in energy and operate at the 14–16% binder level since this normally determines service life. Differences in hydrocarbon binders as typified by polyurethane, polybutadiene-acrylic acid copolymer, polybutadiene-acrylic acid-acrylonitrile terpolymer and carboxy-terminated...
### Table 40
**Properties of Metals**

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>Mg</th>
<th>Al</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>6.94</td>
<td>9.013</td>
<td>10.82</td>
<td>24.32</td>
<td>26.98</td>
<td>91.22</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>180.5</td>
<td>1283</td>
<td>2027</td>
<td>650</td>
<td>659</td>
<td>1855</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>134.7</td>
<td>2484</td>
<td>3677</td>
<td>1108</td>
<td>2467</td>
<td>4474</td>
</tr>
<tr>
<td>Density*, g/cc</td>
<td>.534</td>
<td>.185</td>
<td>2.30</td>
<td>1.74</td>
<td>2.70</td>
<td>6.49</td>
</tr>
<tr>
<td>Specific heat*, cal/g.°C</td>
<td>.848</td>
<td>.436</td>
<td>.261</td>
<td>.244</td>
<td>.216</td>
<td>.067</td>
</tr>
<tr>
<td>Heat of fusion, kcal/mole</td>
<td>.717</td>
<td>2.80</td>
<td>4.60</td>
<td>2.14</td>
<td>2.55</td>
<td>4.89</td>
</tr>
<tr>
<td>Heat of vaporization, kcal/mole</td>
<td>35.16</td>
<td>71.14</td>
<td>121.3</td>
<td>30.56</td>
<td>70.7</td>
<td>136.4</td>
</tr>
</tbody>
</table>

*At ambient temp and press

### Table 41
**Properties of Solid Binary Hydrides**

<table>
<thead>
<tr>
<th></th>
<th>LiH</th>
<th>BeH₂</th>
<th>MgH₂</th>
<th>AlH₃</th>
<th>B₁₁H₁₄</th>
<th>ZrH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>7.948</td>
<td>11.029</td>
<td>26.336</td>
<td>30.004</td>
<td>122.312</td>
<td>93.236</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>686</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>98.78</td>
<td>–</td>
</tr>
<tr>
<td>Decomposition temp, °C</td>
<td>972</td>
<td>240**</td>
<td>280</td>
<td>&gt;100</td>
<td>–</td>
<td>500</td>
</tr>
<tr>
<td>Density*, g/cc</td>
<td>.780</td>
<td>(.7)</td>
<td>1.42</td>
<td>(1.5)</td>
<td>.94</td>
<td>5.67</td>
</tr>
<tr>
<td>Specific heat*, cal/g.°C</td>
<td>.842</td>
<td>–</td>
<td>.321</td>
<td>–</td>
<td>.426</td>
<td>–</td>
</tr>
<tr>
<td>Heat of formation, kcal/mole</td>
<td>-21.63</td>
<td>-1</td>
<td>-18.2</td>
<td>-3</td>
<td>-6.9</td>
<td>-42.4</td>
</tr>
<tr>
<td>Heat of fusion, kcal/mole</td>
<td>7.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.25</td>
<td>–</td>
</tr>
</tbody>
</table>

* At ambient temp and press
** See text
( ) Denotes estimated values

### Table 42
**Properties of Some Complex Hydrides**

<table>
<thead>
<tr>
<th></th>
<th>LiAlH₄</th>
<th>LiBH₄</th>
<th>Be(BH₄)₂</th>
<th>Mg(AlH₄)₂</th>
<th>Al(BH₄)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>37.952</td>
<td>21.792</td>
<td>38.717</td>
<td>86.344</td>
<td>71.536</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>–</td>
<td>280d.</td>
<td>–</td>
<td>–</td>
<td>–64.5</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>–</td>
<td>–</td>
<td>91.3 (sub)</td>
<td>–</td>
<td>44.5</td>
</tr>
<tr>
<td>Decomp temp, °C</td>
<td>137</td>
<td>280</td>
<td>123</td>
<td>140</td>
<td>–</td>
</tr>
<tr>
<td>Density*, g/cc</td>
<td>.917</td>
<td>.66</td>
<td>.604</td>
<td>1.046</td>
<td>.538</td>
</tr>
<tr>
<td>Specific heat*, cal/g.°C</td>
<td>.545</td>
<td>.907</td>
<td>–</td>
<td>–</td>
<td>(.65)</td>
</tr>
<tr>
<td>Heat of formation*, kcal/mole</td>
<td>-28.0</td>
<td>-45.522</td>
<td>-25.8</td>
<td>-36.5</td>
<td>-74.7</td>
</tr>
</tbody>
</table>

*At ambient temp and press
( ) Denotes extrapolated data

### Table 43
**Properties of Nonmetallic Nitrates**

<table>
<thead>
<tr>
<th></th>
<th>NH₄NO₃</th>
<th>N₂H₅NO₃</th>
<th>N₂H₆⁺</th>
<th>NH₃OH⁺</th>
<th>C(NH₄)₂⁺</th>
<th>C(N₂H₅)₂⁺</th>
<th>N₂H₅C⁻</th>
<th>(NO₂)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen, wt %</td>
<td>59.96</td>
<td>50.49</td>
<td>61.12</td>
<td>66.63</td>
<td>39.31</td>
<td>28.72</td>
<td>52.43</td>
<td></td>
</tr>
<tr>
<td>ΔHf, kcal/mole</td>
<td>-87.27</td>
<td>-59</td>
<td>-111</td>
<td>-86.3</td>
<td>-93.0</td>
<td>-11.21</td>
<td>-17.2</td>
<td></td>
</tr>
<tr>
<td>ΔHf, kcal/atom oxygen</td>
<td>-29.1</td>
<td>-19.7</td>
<td>-18.5</td>
<td>-21.6</td>
<td>-31.0</td>
<td>-3.7</td>
<td>-2.9</td>
<td></td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.725</td>
<td>1.685</td>
<td>–</td>
<td>–</td>
<td>1.20</td>
<td>–</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>169.6</td>
<td>70.71</td>
<td>104</td>
<td>48</td>
<td>214</td>
<td>206-216</td>
<td>123d.</td>
<td></td>
</tr>
<tr>
<td>Decomp temp, °C</td>
<td>210</td>
<td>&gt;180</td>
<td>80</td>
<td>&lt;100</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>80.048</td>
<td>95.064</td>
<td>157.080</td>
<td>96.048</td>
<td>122.091</td>
<td>167.139</td>
<td>183.091</td>
<td></td>
</tr>
</tbody>
</table>
### Table 45
Properties of Nitroexplosives

<table>
<thead>
<tr>
<th>Formula</th>
<th>RDX</th>
<th>HMX</th>
<th>TNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point, °C</td>
<td>203.5</td>
<td>276–7</td>
<td>80.6</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>222.129</td>
<td>296.172</td>
<td>227.141</td>
</tr>
<tr>
<td>(\Delta H_{fus}^a) (c), kcal/mole</td>
<td>+14.69</td>
<td>+17.92</td>
<td>–8.6</td>
</tr>
<tr>
<td>(\Delta H_{fus}^b), kcal/mole</td>
<td>–</td>
<td>–</td>
<td>5.09</td>
</tr>
<tr>
<td>Density*, g/cc</td>
<td>1.818</td>
<td>1.903</td>
<td>1.654</td>
</tr>
<tr>
<td>Impact sensitivity</td>
<td>34</td>
<td>(same as RDX)</td>
<td>100</td>
</tr>
<tr>
<td>Bullet impact sensitivity</td>
<td>0</td>
<td>(same as RDX)</td>
<td>100</td>
</tr>
<tr>
<td>Explosion temp, °C</td>
<td>260</td>
<td>337</td>
<td>240</td>
</tr>
<tr>
<td>Activation energy, kcal/mole</td>
<td>47.5</td>
<td>52.7</td>
<td>34.4</td>
</tr>
</tbody>
</table>

*At 25°C

### Table 46
Properties of Glycol Nitrate Esters

<table>
<thead>
<tr>
<th></th>
<th>NG</th>
<th>TMETN</th>
<th>DEGDN</th>
<th>TEGDN</th>
<th>Petrin</th>
<th>BDDN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₃H₅N₂O₉</td>
<td>C₅H₉N₃O₉</td>
<td>C₄H₈N₂O₇</td>
<td>C₆H₁₂N₂O₈</td>
<td>C₂H₉N₃O₁₀</td>
<td>C₄H₈N₃O₇</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>227.097</td>
<td>255.152</td>
<td>196.124</td>
<td>240.178</td>
<td>271.151</td>
<td>180.124</td>
</tr>
<tr>
<td>Freezing pt, °C</td>
<td>13°</td>
<td>2°</td>
<td>2°¹</td>
<td>–19°</td>
<td>–28°</td>
<td>–6 to +11</td>
</tr>
<tr>
<td>(\Delta H_d) kcal/mole</td>
<td>–90.75</td>
<td>–97.8</td>
<td>–103.52</td>
<td>–181.6</td>
<td>–134°</td>
<td>–</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.60</td>
<td>1.47</td>
<td>1.39</td>
<td>1.33</td>
<td>1.54</td>
<td>1.33</td>
</tr>
<tr>
<td>Impact sensitivity</td>
<td>4 BuMines, cm (2kg)</td>
<td>47</td>
<td>100</td>
<td>100</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PicArsn, inches (1 lb)</td>
<td>–</td>
<td>20</td>
<td>9</td>
<td>43</td>
<td>5–10</td>
<td>24</td>
</tr>
</tbody>
</table>

* a Supercools to –50°C
b Commercial product contains DEGDN impurity and freezes at –57°C
c Commercial product freezes at 0–15°C
d At 25°C
e Stable form—labile form freezes at 2°C
f Stable form—labile form freezes at –11°C
polybutadiene polymers influence specific impulse very little (Ref 35). Hence most binder development has been directed at improving physical properties. However, some work has been directed at increasing the energy content in order to operate at the level required to maximize both physical properties and specific impulse. Two approaches have been directed at this. One is to reduce solids loading by incorporating oxygen in the polymer structure; the other is to incorporate the high heat of formation of the acetylenic group into the polymer structure (Ref 34).

The influence of metal type on the specific impulse of propellants has been described previously in this article (Table 16). The max theoretical specific impulse and density impulses ($I_{sp} \times \rho$) for the oxidizers AN, AP, and hydrazinium nitrate with 15 weight percent $\{\text{CH}_2\}_x$ binder have been calculated for various fuels (Ref 24). These data are in Tables 49–51. The $I_{sp}$ performance of nitromagnesium perchlorate, lithium perchlorate and potassium perchlorate and metalized fuels with $\{\text{CH}_2\}_x$ binder are given in Table 52 (Ref 43).
Table 49
Polyethylene (CH₂) as Binder, Ammonium Nitrate (NH₄NO₃) as Oxidizer
15 wt % CH₂

maximum specific impulse (1000 → 14.7 psia)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wt %</th>
<th>Oxidizer</th>
<th>Tc, °K</th>
<th>ρ (g/cc)</th>
<th>Iₚₑ (sec)</th>
<th>ρ Iₚₑ (lb sec/in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>85</td>
<td></td>
<td>1508</td>
<td>1.53</td>
<td>202</td>
<td>11.12</td>
</tr>
<tr>
<td>Li</td>
<td>65</td>
<td></td>
<td>2162</td>
<td>1.09</td>
<td>247</td>
<td>9.747</td>
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<tr>
<td>Be</td>
<td>69</td>
<td></td>
<td>2823</td>
<td>1.54</td>
<td>288</td>
<td>16.03</td>
</tr>
<tr>
<td>Mg</td>
<td>57</td>
<td></td>
<td>2536</td>
<td>1.53</td>
<td>249</td>
<td>13.72</td>
</tr>
<tr>
<td>B</td>
<td>61</td>
<td></td>
<td>2638</td>
<td>1.61</td>
<td>251</td>
<td>14.63</td>
</tr>
<tr>
<td>Al</td>
<td>61</td>
<td></td>
<td>2593</td>
<td>1.65</td>
<td>256</td>
<td>15.25</td>
</tr>
<tr>
<td>LiH</td>
<td>53</td>
<td></td>
<td>1694</td>
<td>1.16</td>
<td>234</td>
<td>9.814</td>
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<tr>
<td>BeH₂</td>
<td>45</td>
<td></td>
<td>2823</td>
<td></td>
<td>333</td>
<td>14.05</td>
</tr>
<tr>
<td>MgH₂</td>
<td>45</td>
<td></td>
<td>2281</td>
<td>1.43</td>
<td>254</td>
<td>13.12</td>
</tr>
<tr>
<td>B₁₀H₁₄</td>
<td>57</td>
<td></td>
<td>2311</td>
<td>1.26</td>
<td>270</td>
<td>12.32</td>
</tr>
<tr>
<td>AlH₃</td>
<td>53</td>
<td></td>
<td>2423</td>
<td>1.52</td>
<td>282</td>
<td>15.55</td>
</tr>
</tbody>
</table>

maximum density impulse (ρ Iₚₑ) (1000 → 14.7 psia)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wt %</th>
<th>Oxidizer</th>
<th>Tc, °K</th>
<th>ρ (g/cc)</th>
<th>Iₚₑ (sec)</th>
<th>Max ρ Iₚₑ (lb sec/in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>85</td>
<td></td>
<td>1508</td>
<td>1.53</td>
<td>202</td>
<td>11.12</td>
</tr>
<tr>
<td>Be</td>
<td>69</td>
<td></td>
<td>2823</td>
<td>1.54</td>
<td>288</td>
<td>16.03</td>
</tr>
<tr>
<td>Mg</td>
<td>57</td>
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<td>15.39</td>
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<td></td>
<td>2423</td>
<td>1.52</td>
<td>282</td>
<td>15.55</td>
</tr>
</tbody>
</table>
Table 50
Polyethylene (–CH₂–) as Binder, Ammonium Perchlorate (NH₄ClO₄) as Oxidizer
15 wt % CH₂

maximum specific impulse (1000 → 14.7 psia)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wt %</th>
<th>Oxidizer</th>
<th>Tₐ, °K</th>
<th>ρ (g/cc)</th>
<th>Max Iₛₚ (sec)</th>
<th>ρ Iₛₚ (lb sec/in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>85</td>
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<td>1.68</td>
<td>240</td>
<td>14.51</td>
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<tr>
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<td>284</td>
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</tr>
<tr>
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<td>258</td>
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<td>265</td>
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<td></td>
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<td>241</td>
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<td>2882</td>
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<td>AlH₃</td>
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<td>271</td>
<td>12.49</td>
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</table>

maximum density impulse (ρ Iₛₚ) (1000 → 14.7 psia)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wt %</th>
<th>Oxidizer</th>
<th>Tₐ, °K</th>
<th>ρ (g/cc)</th>
<th>Max ρ Iₛₚ (lb sec/in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>85</td>
<td></td>
<td>2638</td>
<td>1.68</td>
<td>240</td>
</tr>
<tr>
<td>Mg</td>
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<td>2929</td>
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</tr>
<tr>
<td>B</td>
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<td></td>
<td>2740</td>
<td>1.71</td>
<td>256</td>
</tr>
<tr>
<td>Al</td>
<td>65</td>
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<td>3184</td>
<td>1.76</td>
<td>265</td>
</tr>
<tr>
<td>Be</td>
<td>70</td>
<td></td>
<td>3239</td>
<td>1.66</td>
<td>284</td>
</tr>
<tr>
<td>LiH</td>
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<td></td>
<td>2638</td>
<td>1.68</td>
<td>240</td>
</tr>
<tr>
<td>MgH₂</td>
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<td>2638</td>
<td>1.68</td>
<td>240</td>
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<tr>
<td>B₁₀H₁₄</td>
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<td></td>
<td>2638</td>
<td>1.68</td>
<td>240</td>
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<tr>
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<td></td>
<td>2892</td>
<td>1.63</td>
<td>280</td>
</tr>
<tr>
<td>LiAlH₄</td>
<td>53</td>
<td></td>
<td>2307</td>
<td>1.26</td>
<td>271</td>
</tr>
</tbody>
</table>
# Table 51

**Polyethylene (−CH₂−) as Binder, Hydrazinium Nitrate (N₂H₃NO₃) as Oxidizer**

15 wt % CH₂

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wt %</th>
<th>Oxidizer</th>
<th>Tc, °K</th>
<th>ρ (g/cc)</th>
<th>Max Iₛₚ (sec)</th>
<th>ρ Iₛₚ (lb sec/in³)</th>
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<tr>
<td>none</td>
<td>85</td>
<td></td>
<td></td>
<td>1.50</td>
<td>217</td>
<td>11.73</td>
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<td>1654</td>
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<td>254</td>
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<td>Be</td>
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<td></td>
<td>2166</td>
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<tr>
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<td>255</td>
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</tr>
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<td></td>
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<td>1.63</td>
<td>262</td>
<td>15.44</td>
</tr>
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<td>1.51</td>
<td>284</td>
<td>15.46</td>
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</table>

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wt %</th>
<th>Oxidizer</th>
<th>Tc, °K</th>
<th>ρ (g/cc)</th>
<th>Max Iₛₚ (sec)</th>
<th>ρ Iₛₚ (lb sec/in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>85</td>
<td></td>
<td>1654</td>
<td>1.50</td>
<td>217</td>
<td>11.73</td>
</tr>
<tr>
<td>Be</td>
<td>69</td>
<td></td>
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<td>1.52</td>
<td>289</td>
<td>15.85</td>
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<tr>
<td>Mg</td>
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<td>13.89</td>
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<tr>
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</tr>
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<td>12.56</td>
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<td></td>
<td>2409</td>
<td>1.51</td>
<td>284</td>
<td>15.46</td>
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</table>

# Table 52

**Performance Characteristics of Metallized Solid Propellants**

<table>
<thead>
<tr>
<th>Binder (Wt %)</th>
<th>Additive (Wt %)</th>
<th>Oxidizer</th>
<th>Iₛₚ (sec)</th>
<th>Chamber Temp (°K)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ (20)</td>
<td>Al (15)</td>
<td>NO₂ClO₄</td>
<td>281.5</td>
<td>3894</td>
<td>1.76</td>
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<tr>
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<td>Al (20)</td>
<td>LiClO₄</td>
<td>251.0</td>
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<td>1.97</td>
</tr>
<tr>
<td>CH₃ (14)</td>
<td>Al (16)</td>
<td>KClO₄</td>
<td>228.9</td>
<td>3492</td>
<td>2.04</td>
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<tr>
<td>CH₃ (15)</td>
<td>AlH₃ (25)</td>
<td>NO₂ClO₄</td>
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<td>3783</td>
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<td>AlH₃ (25)</td>
<td>LiClO₄</td>
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<td>1.72</td>
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<tr>
<td>CH₃ (17.5)</td>
<td>LiAlH₄ (20)</td>
<td>NO₂ClO₄</td>
<td>292.4</td>
<td>3507</td>
<td>1.45</td>
</tr>
<tr>
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<td>LiAlH₄ (20)</td>
<td>LiClO₄</td>
<td>237.4</td>
<td>2639</td>
<td>1.54</td>
</tr>
<tr>
<td>CH₃ (25)</td>
<td>Be (8)</td>
<td>NO₂ClO₄</td>
<td>291.2</td>
<td>3270</td>
<td>1.61</td>
</tr>
<tr>
<td>CH₃ (15)</td>
<td>Be (17.5)</td>
<td>LiClO₄</td>
<td>264.9</td>
<td>3453</td>
<td>1.86</td>
</tr>
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<td>CH₃ (17.5)</td>
<td>BeH₂ (17.5)</td>
<td>NO₂ClO₄</td>
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<td>3208</td>
<td>1.34</td>
</tr>
<tr>
<td>CH₃ (20)</td>
<td>BeH₂ (27)</td>
<td>LiClO₄</td>
<td>300.8</td>
<td>2732</td>
<td>1.21</td>
</tr>
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</table>
D. Combustion Instability

The phenomenon of unstable combustion results from a self-amplifying interaction between combustion processes and the acoustic oscillations of the gas within the rocket motor. The unexpected appearance of combustion instability in any rocket generally terminates its mission thru motor case rupture from overpressure, disruption of guidance systems by severe vibration, or thrust malalignment. Both axial mode and transverse mode instabilities are observed (Ref 45). In the case of the transverse mode the characteristic wave time is usually that required to travel radially around the propellant cavity; whereas the characteristic time for the axial mode is the time for the wave to travel from end to end in the combustion chamber. Double-base propellants predominantly are prone to transverse wave instabilities and infrequently to those in the axial mode, while composite propellants appear to go unstable mostly in the axial mode. In the case of transverse instability chamber pressures have been known to double; whereas in axial mode instabilities artificially induced by pulsing the chamber pressure at 1000 psi, the pressure excursion may reach 300–400 psi. A review of recent theoretical combustion modeling for combustion instability has been made by Price (Ref 47).

Experimentally it has been shown that the threshold pressure at which combustion instability can be induced artificially in composite propellants by pulsing is a function of the burning rate of the propellant (in a motor size of 5-inch diameter and 40-inch length) (Ref 45). This relationship is shown in Figs 17 and 18 for both alumined and non-alumined composite propellants. It was also found that potassium perchlorate, lithium perchlorate and AN propellants were resistant to this induced instability. Since AP composites were the only propellants, other than double-base, which were driven unstable, the rate controlling reactions and response function are those related to AP decom and perhaps the diffusion flame between oxidizer and binder.

It can be concluded that if axial combustion instability is observed it can be eliminated by simple ballistic design changes such as propellant burning rate characteristics, motor operating pressure decrease, or a reduction in grain length.
to diameter ratio. In some cases a change in propellant compn has also been found to suppress combustion instabilities. Lead salts have been used to suppress unstable burning in double-base formulations for years. Sayles (Ref 61) has found that double-base compns can be stabilized by adding about 1% weight of polybenzimidazole fibers such as polyphenoxycarboxyphenylbenzimidazole. Other effective additives which have been claimed for polyurethane, nitropolyurethane, polyesteracrylate and rubber-base composite propllnts are finely divided oxides of aluminum, zirconium, silicon, thorium, titanium or lanthanum (Ref 69)

### VII. Explosion Hazards

*Explosion* is a generic term that encompasses *detonation* as well as other phenomena such as LVD (low velocity detonation), accelerating deflagrations, thermal expls, etc. In describing the expln hazards of SP we will confine ourselves to SP detonations and to deflagration-to-detonation transitions (DDT). We do this because we know of no LVD phenomena in SP, and thermal expls are no different from thermal expls in high explosives (HE) and have been described previously (Vol 7, H39-R, H170–73 and K12-L; and Vol 4, D619-L)

### Table 53

**Detonation Characteristics of Solid Propellants**

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Density (g/cc)</th>
<th>Diameter (cm)</th>
<th>Critical Diameter (cm)</th>
<th>Detonation Velocity (km/sec)</th>
<th>Detonation Pressure (kbar)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB 40/60 NG/NC</td>
<td>1.0</td>
<td>8–10</td>
<td>0.3(a)</td>
<td>5.45</td>
<td>90–93</td>
<td>46b</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>6</td>
<td></td>
<td>6.40 (b)</td>
<td>–</td>
<td>46b</td>
</tr>
<tr>
<td></td>
<td>1.63</td>
<td>–</td>
<td>0.8–1.0</td>
<td>7.60</td>
<td>–</td>
<td>46b</td>
</tr>
<tr>
<td>NC rifle powder</td>
<td>0.79</td>
<td>2.6–3.0 (c)</td>
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<td>3.80</td>
<td>–</td>
<td>46a</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>2.6–3.0 (c)</td>
<td>–</td>
<td>5.30</td>
<td>–</td>
<td>46a</td>
</tr>
<tr>
<td>NC cannon powder</td>
<td>1.45</td>
<td>–</td>
<td>–</td>
<td>7.01</td>
<td>–</td>
<td>46a</td>
</tr>
<tr>
<td>Uncolloided NC powder</td>
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<td>0.8</td>
<td>–</td>
<td>2.3–2.4</td>
<td>–</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.8</td>
<td>–</td>
<td>2.7</td>
<td>–</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.82</td>
<td>0.8</td>
<td>–</td>
<td>2.9</td>
<td>–</td>
<td>17</td>
</tr>
<tr>
<td>NC/NG Ballistite</td>
<td>1.53</td>
<td>0.8</td>
<td>–</td>
<td>7.4–7.6</td>
<td>–</td>
<td>46a</td>
</tr>
<tr>
<td>AP/Al/PBAN (d)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>with 9.2% RDX</td>
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<td>–</td>
<td>6.9</td>
<td>–</td>
<td>–</td>
<td>36b</td>
</tr>
<tr>
<td>with 7.1% RDX</td>
<td>–</td>
<td>–</td>
<td>13.2</td>
<td>–</td>
<td>–</td>
<td>36b</td>
</tr>
<tr>
<td>with 4.75% RDX</td>
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<td>–</td>
<td>28.2</td>
<td>–</td>
<td>–</td>
<td>36b</td>
</tr>
<tr>
<td>90/10 AP/Wax</td>
<td>0.93</td>
<td>7.62</td>
<td>&gt; 0.65 (e)</td>
<td>4.07</td>
<td>–</td>
<td>69a</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>7.62</td>
<td>&gt; 0.65 (e)</td>
<td>4.54</td>
<td>–</td>
<td>69a</td>
</tr>
<tr>
<td></td>
<td>1.52</td>
<td>–</td>
<td>&gt; 0.5</td>
<td>–</td>
<td>–</td>
<td>69a</td>
</tr>
<tr>
<td>80/20 AP/Wax</td>
<td>0.91</td>
<td>7.62</td>
<td>&gt; 0.65 (e)</td>
<td>4.48</td>
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<td>69a</td>
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<tr>
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<td>1.10</td>
<td>–</td>
<td>&gt; 0.95 (f)</td>
<td>4.79</td>
<td>–</td>
<td>69a</td>
</tr>
<tr>
<td></td>
<td>1.40</td>
<td>–</td>
<td>&gt; 0.5</td>
<td>–</td>
<td>–</td>
<td>69a</td>
</tr>
</tbody>
</table>

(a) 0.43mm–diameter spheres  
(b) Disks  
(c) Confined in iron pipes of this diameter  
(d) PBAN = polybutadiene-acrylonitrile copolymer  
(e) But ≤ 0.95cm  
(f) But ≤ 1.27cm
Solid propmts appropriately initiated have many of the detonation characteristics of HE. This is illustrated in Table 53, where it will be noted that the detonation velocity of SP increases with density and charge diameter similarly to that observed with HE. However, there are differences. In general, critical diameters (diameters below which no stable detonation propagates) are larger for SP than for HE. Furthermore, critical diameters for composites increase with increasing charge density (See Fig 19), whereas for most HE (and apparently for double-base propmts – see Table 53) critical diameters decrease with increasing charge density. For well-compacted composites critical diameters tend to become very large. For some composite propmts the detonation velocity-density curve has a max even at infinite diameter (See Fig 20). This has also been observed for some aluminized HE, but not for single-component HE or HE mixts such as Comp B, Pentolite etc.

Detonation in SP is initiated by shock or by DDT (deflagration to detonation transition). Let us first examine shock initiation, i.e., initiation by in-contact or close-by detonation of HE or other proplnt, or by high-velocity impact by a bullet, flying plate, or fragment.

For a quantitative determmtion of the shock required to initiate a SP one needs the Hugoniot for that particular proplnt (see Vol 7, H179-83 and 156). Hugoniot relations for several SP are givrn in Table 54. These data, transposed into the P-u form of the Hugoniot, can be used to obtain incident shock pressures in SP regardless of whether the shock originates in a nearby detonation (eg., in a “gap test” or in a high velocity impact (eg., impact by a flying plate).

Threshold shock pressures to initiate detonation in several SP are shown in Table 55. In general, unless the SP contains solid HE ingredients such as HMX or RDX, the threshold pressures are considerably greater than for solid HE at a comparable degree of compaction. Even so, the pseudo-composites of AP/wax must be considered to be rather shock-sensitive provided their degree of compaction does not exceed about 90% of their theoretical max density (TMD). Figure 21 shows that up to about 90% TMD the shock sensitivity of an 80/20 AP/wax composite is very similar to that of TNT.
Table 54
Hugoniot Equations for Several Solid Propellants

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Density (g/cc)</th>
<th>Hugoniot</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>EJC, NG/NC/AP/Al/HMX/plastic</td>
<td>1.80</td>
<td>( U = 1.724 + 2.55u )</td>
<td>40a</td>
</tr>
<tr>
<td>FFP AP/Al/binder</td>
<td>1.76</td>
<td>( U = 1.327 + 2.43u )</td>
<td>40a</td>
</tr>
<tr>
<td>PBAN-170 – 27.7/15/16.8/0.5</td>
<td>1.69</td>
<td>( U = 2.29 + 1.67u )</td>
<td>47a</td>
</tr>
<tr>
<td>AP/Al/PBAN-Terpolymer/Fe₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NB Ballistite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60/40 NC/NG</td>
<td>1.63</td>
<td>( U = 1.70 + 1.85u )</td>
<td>52a</td>
</tr>
<tr>
<td>60/40 NC/NG</td>
<td>1.00</td>
<td>( U = 0.58 + 1.68u )</td>
<td>52a</td>
</tr>
</tbody>
</table>

Table 55
Shock Sensitivity of Several Unconfined Propellants

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Diameter (cm)</th>
<th>Density (g/cc)</th>
<th>Threshold Pressure (kbar)</th>
<th>Detonation Velocity (m/sec)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>EJC (a)</td>
<td>2.54</td>
<td>1.80</td>
<td>( \leq 562 ) (b)</td>
<td>7800</td>
<td>39a</td>
</tr>
<tr>
<td>FFP (a)</td>
<td>2.54</td>
<td>1.76</td>
<td>( &gt; 80 ) (b)</td>
<td>Burned</td>
<td>39a</td>
</tr>
<tr>
<td>PBAN-170 (a)</td>
<td>5.08</td>
<td>1.69</td>
<td>( &gt; 120 ) (c)</td>
<td>Burned</td>
<td>47a</td>
</tr>
<tr>
<td>90/10 25μ AP/wax</td>
<td>5.08</td>
<td>1.60</td>
<td>40–46 (c) (d)</td>
<td>Detonated</td>
<td>69a</td>
</tr>
<tr>
<td>90/10 25μ AP/wax</td>
<td>5.08</td>
<td>1.52</td>
<td>20 (c) (d)</td>
<td>Detonated</td>
<td>69a</td>
</tr>
<tr>
<td>80/20 200μ AP/wax</td>
<td>5.08</td>
<td>1.50</td>
<td>22 (c) (d)</td>
<td>Detonated</td>
<td>69a</td>
</tr>
<tr>
<td>AP/Al/PBAN with 9.2% RDX</td>
<td>30.2</td>
<td>–</td>
<td>20 (c)</td>
<td>Detonated</td>
<td>36b</td>
</tr>
<tr>
<td>Same with 7.4% RDX</td>
<td>38</td>
<td>–</td>
<td>19 (c)</td>
<td>Detonated</td>
<td>36b</td>
</tr>
<tr>
<td>Same with 4.75% RDX</td>
<td>40.8</td>
<td>–</td>
<td>15 (c)</td>
<td>Detonated</td>
<td>36b</td>
</tr>
<tr>
<td>Powder N (compn not given)</td>
<td>2–3</td>
<td>1.58</td>
<td>86 (b)</td>
<td>Detonated</td>
<td>25a</td>
</tr>
</tbody>
</table>

(a) See Table 54
(b) Plane-wave donor
(c) NOL gap test geometry
(d) 50% point; pressure in Lucite attenuator at Lucite-sample interface

Fig 21 Shock sensitivity curves for waxed and unwaxed ammonium perchlorate and for TNT. Vertical lines at top of graph mark lowest percentage of TMD at which a sub-detonation reaction was observed (Ref. 69a)
Let us now examine DDT. The latest and also the most penetrating studies of DDT were with HE rather than SP. However, there is every expectation that DDT in HE and SP are similar, with only minor differences.

Modern studies (Refs 20, 49a, 49b, 55a, 69a & 69b) have stressed the importance of a convective flame front in establishing DDT in granular explosives. A convective flame front is an ignition wave which is propagated by the passage of hot combustion gases thru the pores of the charge. The hot gases are forced into the pores because of confinement at the igniter end of the container. However, penetration of the gases into the charge does not occur immediately in the formation of a convective flame front. The gases heat the pore walls and are consequently cooled themselves. It is the continuous flow of gases which raises the temp of the pore walls until ignition in the pores occurs and produces what is now the head of the convective front.

Bernecker & Price (B & P) (Ref 69a) present strong evidence for the convective flame front—DDT mechanism sketched in Fig 22 and summarized as follows:

"Granular charges of 91/9 RDX/wax have exhibited a transition from deflagration to detonation in compactions of 67 to 95% TMD (theoretical maximum density). Processes observed in such transitions are local ignition by an igniter mix, general ignition by a convective flame front, compaction of the more porous burning beds, formation of a post-convective (compressive) wave which marks the beginning of accelerated pressure buildups, subsequent coalescence of compressive waves into a shock, and finally a shock to detonation transition." The compressive phenomena leading to shock formation cannot be detected optically and have not been reported in earlier literature (eg, in Refs 20, 49a & 49b).

In a later publication (Ref 69b) B & P expand their model of DDT to explain the observed variation of predetonation run-up distance with degree of compaction and particle size in terms of charge column permeability. They characterize permeability by B_0 (in cm^2), the permeability coefficient of the Darcy equation. For TMD ≤ 70–80%, log B_0 is a linear function of TMD for granular PETN and TNT. B & P define a B_0_crit as the value of B_0 below which the log B_0 vs TMD curve is no longer linear, ie, the point beyond which the permeability of the column begins to decrease rapidly with increasing TMD. Then they proceed to discuss DDT in terms of B_0 and B_0_crit in the following manner:

"Case A: Impermeable Charges"

1. 100% TMD and Cast Charges. At crystal density (100% TMD) there is no porosity and, of course, the charge is impermeable; the latter is also true for cast charges. Hence, the ability of the expl to undergo DDT will be determined by the criteria outlined in Refs 19 & 36a.

To summarize briefly, (a) there must be a sufficiently rapid pressure rise in the ignition region caused by the generation of high product gas pressures, and (b) the unburned expl beyond the ignition region must be sufficiently sensitive to be-initiated by a shock wave equal in amplitude to the high pressures generated near the igniter. Consequently, the distance to the onset of detonation, x, decreases as d^2p/dt^2 increases.

The first criterion, (a), which pertains to the burning area of the charge could be more mean-
ingfully described in terms of an energy per unit volume concept. We define \( \psi_b \) as the energy per unit volume in the solid phase and \( \psi_g \) as the energy per unit volume in the gas phase. Thus, the first criterion could be reworded, for our discussion, to require that \( d\psi_g/dt \) increase rapidly enough to effect DDT for cast materials. The energy per unit volume in the gas phase will be determined by (1) the energy available in the expl (proportional to \( \psi_b \); this depends upon the chemical composition and compaction); (2) the rate at which this energy is released (proportional to \( -d\psi_g/dt \); this depends upon the linear burning rate); and (3) the rate at which energy is lost from the ignition region (this depends upon losses to the walls, hot gases flowing out of the burning region due to permeability, either natural as in porous charges or accidental as in poorly prepared charges having air cavities or cracks).

2. Charges with \( B_0 \ll B_0^{\text{crit}} \). The introduction of porosity into a charge does not mean that the charge will be permeable. The pores may or may not be interconnected. If the pores are not connected, permeability is very low and essentially negligible. The criteria for DDT in this subsection will be the same as discussed for Case A(1). We would expect \( \ell \) to be smaller than in Case A(1) because the porosity will slightly enhance \( dp/dt \) and because the critical shock initiation pressure for detonation, \( P_i \), would be slightly lower. If the expl does not undergo DDT at 100% TMD or as a cast material, it probably will not undergo DDT at these densities either. This will probably be the case for very highly waxed RDX.

Case B: Charge Densities where \( B_0 \leq B_0^{\text{crit}} \)

As the porosity increases, the fraction of pores which are interconnected increases rapidly. However, the permeability of the charge will be small. The formation of an ignition front in the pores of the expl (convective burning) can now occur and will depend upon the permeability of the charge, the adiabatic flame temp of the expl, the ignition characteristics of the expl and the ability of the confinement to allow a critical "driving" pressure to be set up. The onset of convective burning indicates that non-negligible amounts of energy can be transported by gas flow beyond the ignition region. However, for these densities (where \( B_0 < B_0^{\text{crit}} \)) only very small quantities of gas can flow out of the ignition area over a time period as long as 100 \( \mu \)sec. Even so \( d\psi_g/dt \) in the igniter region should be larger for Case B than for Case A because a larger surface area for additional burning has been introduced by the interconnected pores. Thus, \( \ell \) should decrease in the order: Case A(1) — Case A(2) — Case B.

The mechanism for DDT in this case is very similar to that in cast expls, the chief difference is the proposed initiation by a convective flame front.

Case C: Charge Densities where \( B_0 > B_0^{\text{crit}} \)

As more porosity is introduced into the charge, the gas flow can no longer be described as choked. Enough pores are connected to permit flow which may be described as steady state. The increased permeability for this case leads to smaller values of \( dp/dt \) (ie, \( d\psi_g/dt \)) and \( \psi_b \). The time required to produce a rapid increase in \( dp/dt \) is longer than in Cases A and B since more expl must be burned to compensate for the energy flow (in the gas phase) out of the burning area.

The point (distance from the igniter/explosive interface, \( x \)) at which this rapid increase in \( dp/dt \) occurs may be farther from \( x = 0 \) (at a point farther away from the igniter interface and in the pores of the granular bed) than in cases above. Within the density range of Case C, \( dp/dt \) should increase with increasing porosity because of increasing permeability and smaller values of \( \psi_b \) as mentioned above. The position of onset of detonation should henceforth increase with increasing porosity. Our expl results have indicated that a buildup to DDT begins only after the pressure in the ignition region begins to accelerate (ie, is capable of sending out strong compressive waves).

The DDT mechanism for this case is similar but not identical to that of Case B. A convective flame front propagates ahead of the compressive waves which are necessary to form a precursor shock front. In modeling DDT the convective front (and its consequences) must be included because of its influence on \( dp/dt \) in the ignition region.

Case D: Very Permeable Charges; \( B_0 >> B_0^{\text{crit}} \)

For the very permeable charges (\( B_0 >> B_0^{\text{crit}} \)), \( \ell \) increases with increasing porosity in accord with the discussion in Case C. However, the
energy losses from the burning region near the igniter can be large enough to prevent the attainment of a sufficiently large $dV_c/\text{dt}$ (or $dp/\text{dt}$) to effect transition. Hence, the burning area is now a large region beyond the igniter area. For expls like RDX this will be the case for charges with very large porosities and it will occur at lower porosities for less energetic expls, such as 91/9 RDX/wax. Thus, in Case D the chemical compn and the linear (conductive) burning rate (as reflected in $\psi_b$ and $d\psi_b/\text{dt}$, respectively) become increasingly important. For the more energy deficient expls, such as ammonium picrate, pressure increases at these densities can be quite slow and nonaccelerating. The absence of an increasing $dp/\text{dt}$ does not mean the absence of a high pressure. Pressure may increase linearly to several kilobars but in the absence of a rapidly rising $dp/\text{dt}$ no strong compressive waves emanate from the burning region.

When an increasing $dp/\text{dt}$ does not occur, the pressure and pressure gradient generated in the burning region are sufficient to initiate movement of the porous bed after a period of one to two hundred microseconds. Consequently, collapse of the porous structure occurs immediately beyond the edge of the burning bed (nearest the igniter). This collapse process increases the available energy per unit volume in the compacted material (ie, $\psi_b$) and here an increasing $d\psi_b/\text{dt}$ can be attained if it could be attained at higher densities (ie, Case C). If an increasing $d\psi_b/\text{dt}$ was not observed at higher densities, it may still result after pore collapse because the temp of the collapsed bed will be higher than that of the initially higher density cases.

The DDT mechanism for Case D is identical to that proposed for Case C. However, the model for DDT in Case D will differ from that of Case C because of compaction of the porous bed.

If from the above discussion the variation of $\xi$ is traced from case to case, it is seen that a minimum in the $\xi$-compaction plane is a natural consequence of the effects of permeability and the proposed driving force for DDT.

The above model for DDT is based on expl observation with granular and cast HE. However, as already mentioned, DDT in SP and HE should have many similarities. This contention is supported by the observations of Roth (Ref 17) and Wachtel (Ref 29a). Roth’s smoke camera pictures of an uncolloided single base smokeless powder at low compaction are very similar to the smear records of PETN, RDX, HMX and Tetryl obtained by Griffiths & Grooock (Ref 20), or RDX records obtained by Calzia (Ref 52b). Wachtel showed that closed bomb burning behavior of Comb B & TNT is similar to that of a double-base propmt with a solid oxidizer, or a high energy double-base propmt, or a composite double-base propmt made by Rohm & Haas.

Wachtel (Ref 29a) also points out the tendency of composite propmts to undergo brittle fracture when stress is applied to them at high strain rates. This tendency is accentuated by low ambient temps, and it is known that cannon and rocket propmts have a greater tendency to detonate at low ambient temps than at normal temps. Along similar lines, Frolov et al (Ref 55a) hypothesize that the chance of detonating SP increases if burning of the SP tends to produce collisional flow (jets) which enhances convective burning. Collisional flow is more likely to occur in non-uniform systems. Thus homogeneity of dispersion of the solid material in the binder may be an important safeguard against DDT in composite propmts.

VIII. Brief Summaries of Recent Literature on Solid Propellants

The following are somewhat subjective selections from the vast amount of recent published material on solid propellants. These short abstracts are grouped under the headings of: ignition, combustion, reactivity, detonability & safety, analytical procedures & data, and miscellaneous. In each grouping the abstracts are arranged chronologically.

Ignition:

Mantoro Uetake & Hiroshi Sata, Kogyo-KayakuKyokaishi 24(2), 67–72 (1963), and CA 60, 11835 (1964): Propmts (I) fail to ignite when the elec resistance in the discharge circuit is too high. There is an optimum resistance value to ignite I. When the spark voltage is high, the range of resistance of I is wider. The energy to ignite I is larger than that for gas. The min measured energy is 10 millijoules for the ignition of I. The min electrostatic voltage for ignition is about 800V, and at smaller voltages...
I do not ignite. The form of the electrode affects the probability of ignition of I. Double-base propellants are more liable to ignite by electrostatic spark than single-base propellants. Graphite-coated I are very difficult to ignite. The ignition probabilities depend upon the particle sizes of I and the smaller the particle size, the higher the probability becomes and vice versa. The mechanism of ignition is considered as follows: I are decomposed by the elec spark and produce ignitable gases; the gas ignites, and then the gas flame ignites the solid propellant. Consequently, crit time and spark are required for I to produce inflammable gas which follows burning of the propellant.

H. Wise, S.H. Inami & L. McCulley, Combust-Flame 11(6), 483–88 (1967) & CA 68, 61006 (1968): The contribution of exothermic, condensed-phase reactions to ignition and deflagration of propellants is examined. Measurements of the rates of heat release, thermal diffusivity, burning rate and ignition are combined to demonstrate the role of reactions in propellants made up of powd AP and catalysts. By means of a theoretical analysis, it is found that for the propellants under study a thermal runaway in the condensed phase can account for the ignition phenomena observed. Also, at low steady-state deflagration rates the contribution of the solid-phase reactions can be demonstrated. Some of the propellants quenched during deflagration showed the existence of a subsurface layer, which is located in a zone at which the temp reached the level characteristic of the crystal transition of AP.

J. Pantoflický, and Frantisek Lebr, Combust-Flame 11(6), 464–70 (1967) & CA 68, 61107 (1968): A method for measuring the ignition energy of propellants using hot wires at high heat fluxes is described and the influence of pressure, propellant temp and ignition time is determined. Several experiments showed good reproducibility of results using the equipment proposed. The difference between ignition at high and low heat fluxes is discussed. A method for correcting ignition energy with respect to the wire diam is proposed.

M. Barrere, RechAerosp No 123, 15–28 (1968) & CA 70, 69707 (1969): Static and dynamic methods for studying the ignition of solid-propellant rockets are described. The principal parameters affecting the ignition are the level of energy required for inflammation, the nature of the gas surrounding the sample, the gas pressure, the gas velocity near the surface, the temp of the propellant, its nature, and the effect of catalysts. The nature of the oxidizer, geometry of the grain, internal ballistics of the igniting app, and the mechanism of ignition of the propellant block were studied and an analysis made of the pressure rise during ignition. Study of ignition of the propellant includes a study of the evolution of gas in the central canal, heat transfer to the wall, flame propagation, etc.

C.H. Waldman & M. Summerfield, AIAA J 7(7), 1359 (1969) & CA 71, 126689 (1969): In the theoretical prediction of the ignition delay when a condensed fuel is brought in contact with a hot reactive gas, a math model based on the assumption that the initiating exothermic reaction is a heterogeneous one on the fuel surface is compared with a model based on the assumption that the initiating reaction takes place in the thin vapor boundary layer after vaporization. Curves based on both assumptions give similar predictions. Both predict that the total pressure is approx inversely proportional to the partial pressure of the oxygen in the test gas, and that the ignition delay is shortened when the total pressure is increased by a nonoxidizing neutral gas.


L.J. Shannon, AIAA J 3(2), 346–53 (1970) & CA 72, 113370 (1970): Ignition characteristics of representative composite solid propellants were studied by using an arc-imaging furnace to provide a radiant-energy source. The variation of propellant ignitability with formulation changes was small, provided the binder and oxidizer were fixed. The min initial pressure for which ignition occurs is predominantly detd by the thermal decomps characteristics of the binder compnent in AP-based propellants. It is proposed that a key step required to achieve ignition is establishment of a crit gas-phase reaction rate threshold adjacent to the propellant surface.

Previous theoretical studies of gas-phase ignition of homogeneous solid propellants under shock-tube conditions, the ignition criteria have been related to some specific character of the temp distribution in the gas phase. Correspondence of the exptl criteria involving detection of light emission was uncertain. A new theoretical criterion has been developed, relating the light energy received by a photocell to the transient gas-phase distribution of reaction products and temp. Light emission and ignition characteristics found by using this criterion agree quite closely with exptl results. Investigation of ignition behavior for different relative reactivities of the ambient gaseous oxidizer indicate progressively less effect of the ambient gaseous oxidizer mole fraction on the ignition delay as the relative reactivity of the evolved oxidizer increases.

W.H. Andersen, CombustSciTechnol 5(1), 43–46 (1972) & CA 76, 115652 (1972): A kinetic analysis of the published surface-ignition behavior of M2 double-base propellants is made by using a recently developed approx analytical model that assumes ignition to result from an adiabatic, 1st-order surface reaction. Values of the kinetic parameters obtained in the analysis are the same as those obtained by using the results of numerical soln of the more rigorous ignition equations given in the literature. This agreement provides further support for the general validity of the analytical model. The manner of analyzing exptl data with the analytical model is described in detail.

A. Linan & A. Crespo, USNatTechInformServ, AD Rep No 751303 (1972) & CA 78, 99963 (1973): An asymptotic analysis within limits of large activation energies is presented for ignition of a solid propellt undergoing an exothermic heterogeneous Arrhenius reaction with a gaseous oxidizer. The analysis was conducted for hypergolic or shock-tube ignition conditions and also for ignition under a radiant flux with in-depth absorption of the radiation. The analysis shows that the thermal runaway follows a much longer inert heating stage. A closed-form expression relates the ignition characteristics. An analytical expression was also found for ignition time under hypergolic or shock-tube ignition conditions.

P. Larue & L. Nadaud, RechAerosp 6, 297–311 (1972) & CA 78, 161664 (1973): Visuali-

zation of combustion by color photog and pressure measurements were used to determine the time necessary to reach self-sustaining combustion and the pressure rise in the combustion chamber after ignition of the grains. The first phase consists of establishment of contact between hot gases from the igniter and the propellt surface, heating, and chemical reaction by pyrolysis without flames, followed by visible radiation. The igniter flow rate is related to the pressure buildup and the min flow rate below which ignition will not take place is defined. The lower the ignition flow rate, the longer the ignition time and the faster the pressure buildup after ignition. The max duration of self-sustaining combustion is also defined.

N.P. Suh, J.P. Picard & C. Lenchitz, USNatTechInformServ, AD 756880 (1972) & CA 79, 116696 (1973): The mechanisms of ignition and deflagration of NC-based propellants are described. The propellt behaves like an inert solid during the preignition heating stage. The solid-phase reaction becomes important during steady-state deflagration at low pressures, especially in single-based propellants because of their slow gas-phase reactions. During both the ignition and deflagration, the heat transported from the gas-phase reaction zones to the solid surface sustains the decomn of the solid phase. The modes of heat transfer between the gas-phase zones and the solid-phase reactions are discussed, including the contribution of thermomechanical effects.

V.F. Mikheev & Yu.V. Levashov, FizGornyiya-Vzryva 4, 506–10 (1973) & CA 80, 28968 (1974): The effects of heat flux on burning propellants were investigated. In three series of expts, crit time of interruption of light flux during ignition, the crit heating time during stationary burning, and the crit amplitudes of the emission of a constant-burning propellants were determined. A nitroglycerine propellt (I) and the same propellt with soot (I + soot) were used. The heat emission intensity (from a graphite furnace at ~2000°) was ~0.01 cal/cm²-sec. The samples were cylinders 20mm in diam and 20mm high. In the first series of expts, they were exposed to light flux of a given intensity (qa) until ignition, τ_q, and for a short time (Δτ_i) after ignition. At the end of time τ = τ_q + Δτ_i, the light was interrupted and the action of the burning propellt (burning or ex-
tinction) was plotted vs $q_o$. At $q_o = 1$ cal/(cm$^2$-sec), the propalt continued to burn steadily. With increasing $q_o$, the critical time of interruption decreased. In the second series of expts, the samples were ignited by a glowing spiral and after 3–5 sec (when stationary burning was established) the propalt was exposed to a light flux of known intensity for various times ($\Delta \tau_b$). The $\Delta \tau_b$ vs $q_o$ curves separated the region of stable burning from the extinction region. The lower limits of $q_o$ for steady burning were about 1 and about 2 cal/(cm$^2$-sec) for I + soot and I respectively. In the third series, the samples were initiated by a glowing spiral and burned on being exposed to light of a given intensity. After 4–10 secs (when stationary burning was established), the light flux was interrupted and the reaction of the burning propalt to the interruption of light was recorded. For the I + soot, critical values of $q_o$ were 1 and 1.5 cal/(cm$^2$-sec) at initial temps of 20 and 100$^\circ$ respectively. For I the critical value of $q_o = 2$ cal/(cm$^2$-sec)

**Combustion:**

W.G. Brownlee, AIAA, Los Angeles, Calif., Paper No 63-228 & CA 61, 6849 (1964): Information is obtained concerning the effects of varying the operating pressure level, grain cross section, motor diameter and length, and associated area ratios. Various Al powders are substituted for a portion of the propalt oxidizer, and LiF is added in one instance. Use of a new pulse technique for the injection of flow disturbance at the head end of the motors permits command triggering of instability. The time average (unstable) chamber pressure is strongly dependent on the restriction ratio. Use of an exptl stability parameter in design prediction depends on a knowledge of scaling factors. A 2-inch diameter motor is more unstable than an 8-inch motor, while limited results from 8- and 17-inch motors are in general agreement. The addition of Al powder to the propalt does not suppress axial instability. All propalts tested, including one with 19% Al, could support instability at sufficiently high values of restriction ratio. The results indicate that the crit pressure level is higher for faster-burning propalts. The stable burning rate of one aluminized propalt is reduced by incorporating 1.8 parts of LiF. This modification reduces the crit pressure level drastically and leads to a propalt that is capable of extremely violent instability at practicable restriction-ratio levels. The results and techniques described were applied to the design and testing of a motor for the Black Brant vehicle.

J. Powlng & W.A.W. Smith, 10th Symp-Combust, 1373–80 (1964) & CA 63, 17782 (1965): Burning surface temps have been measured for fuel-weak AP-parafomaldehyde mixts at pressures up to 300 psia by using an IR emission technique. Temp measurements up to 60 psia were reasonably reproducible, and the values were compatible with the existence, at the surface, of an equilibrium between solid AP and the gaseous depn products NH$_3$ and HClO$_4$. Results above 60 psia were rather erratic, and exptl failure to eliminate the variations led to a reappraisal of the optical method for measuring surface temps. The temp gradients within the solid became too steep at these pressures even for this method, which can see as little as 2$\mu$ of surface depth.

A.F. Belyaev et al, NauchnTekhnProbiGoreniya i Vzryva (1965), (1), 25–30 & CA 63, 17784 (1965): The burning rates of various mixts of solid oxidizers and fuels were measured at less than 1 atm. Four stoichiometric mixts (AP + TNT, KClO$_4$ + TNT, AP + bitumen, and AP + paraformaldehyde) and systems containing 80% AP and 20% mixts of polystyrene with polyesters were investigated. The particle size of the comps was 10–20$\mu$. The density of mixts was about 98% of the theoretically possible density. Relations between burning rate (u) and pressure (p) are presented in diagrams. For all the mixts tested, the relation between u and p satisfied the equation $u = bp$. When the particle size of the oxidizer was 250$\mu$, the equation was $u^p = p^0.7$. The discussion of the burning mechanism leads to the conclusion, however, that the relation between u and p cannot always be characterized by a simplified linear equation.

F.L. Schuyler & T.P. Torda, AIAA J 4 (12), 2171–7 (1966) & CA 66, 3063 (1967): Steady-state combustion of solid double-base and mono-propl rocket was investigated analytically. The nonlinear differential equations describing the motion of a laminar 2-dimensional, compressible, chemically reacting viscous fluid are intimately coupled with the 1-dimensional
heat-conduction equation of a burning solid propellant, and the 1-dimensional, compressible, inviscid flow of combustion products thru the central core of the propellant grain. Application of numerical methods and use of realistic rocket conditions as input showed that calcd propellant burning rates and wall temps fall within the range of previously obtained expnl values. In addition a study of the effect of various parameters on the combustion process showed that:
(1) the chem reaction rate and heat of combustion have the greatest effect on the heat flux to the propellant; (2) the axial gas velocity has the greatest effect on the propellant surface shear stress; (3) the activation energy in the pyrolysis-rate expression together with the chem reaction rate have the greatest effect on the propellant burning rate; and (4) the gas-phase sp heat at const pressure, the frequency factor in the pyrolysis rate expression, and the propellant heat of devt have only a secondary influence on the combustion process.

A project designed to gain an understanding of the mechanism of action of ballistic modifiers in NC-based propellants was carried out. A study was undertaken to investigate the feasibility of using mass spectrometry to follow the reactions occurring on the decomposing surface of solid propellant grains. A special low-pressure arc-image strand burner was designed and fabricated for monitoring on the New York University Mass Spectrometer. The spectrometer is a 60° sector fast-scan machine allowing 1000 sweeps/sec with an accuracy on simple mixts with interfering peaks between 0.05 and 1.0%. The equipment worked extremely well; should be suitable for studying a wide range of solid propellants. A number of unstable species and free radicals were found, especially NO₂⁻, CH₃CO⁻, and CHO⁻. These species were not only detected during and after "burning", but also were detected prior to any visual indications of devt. Preliminary data indicate that Pb catalysts increase the rate of oxid-rexn reactions between CH₃CO⁻ and NO₂⁻.

S.S. Novikov et al, DoklAkadNauk SSSR 174 (5), 1129–31 (1967) & CA 67, 83549 (1967): The combustion of nonrandom and random mixts of Plexiglas and powered KClO₄ was studied at 1–60 atm. The nonrandom mixts were prepared by milling slots in a Plexiglas block and packing the slots with KClO₄. The thickness of the Plexiglas barrier between the layers of KClO₄ was 0.35–0.5mm. The random mixts were prepared from Plexiglas particles 0.4mm in diam and had the same overall fuel/oxidizer ratio as the nonrandom mixts. At 1 atm, only the random mixts could be ignited, but they burned unstably. Above 5 atm, both mixts burned stably. At about 5 atm, the random mixts burned at only half the rate of the nonrandom mixts; but, with increasing pressure, their burning rates increased. However, the rate did not remain constant. It was concluded that in random mixts there is a sharp increase in contact between fuel and oxidizer in the layer adjacent to the burning surface, which leads to increased heat liberation and a corresponding increase in burning rate. However, since the heat and mass transfer into the gas phase are nonuniform, this must lead to a decrease in burning rate and to nonsteady-state conditions.


H. Krier et al, AIAA J 6 (2), 278–85 (1968) & CA 68, 61103 (1968): Nonsteady burning of solid propellants is being investigated both theoretically and exply with attention to combustion instability, transient burning during motor ignition, and extinction by depressurization. The theory is based on a one-dimensional model of the combustion zone consisting of a thin gaseous flame and a solid heat-up zone. The nonsteady gaseous flame behavior is deduced from experimental steady-burning characteristics; the response of the solid phase is described by the time-dependent Fourier equation. Solutions were obtained for dynamic burning rate, flame temp, and burnt gas entropy under different pressure variations; two methods were employed. First, the equations were linearized and solved by standard techniques. Then, to observe nonlinear effects, solutions were obtained by digital computer for prescribed pressure variations. One significant result is that a propellant with a large heat evolution at the surface is intrinsically
unstable under dynamic conditions even though the gas entropy amplitude and phase depend critically on the frequency of pressure oscillation and that either near-isentropic or near-isothermal oscillations may be observable. Expts with an oscillating combustion chamber and with a special combustor equipped for sudden pressurization tend to support the latter conclusion.

J.B. Anderson & R.E. Reichenbach, AIAA J 6 (2), 272–77 (1968) & CA 68, 61104 (1968): The average burning rates of composite solid rocket propellants were measured in acceleration fields up to 2000 times the standard acceleration of gravity. The acceleration vector was perpendicular to and into the burning surface. Propellant strands were burned in a combustion bomb mounted in a centrifuge, and surge tanks were employed to insure essentially constant pressure burning at 500, 1000 and 1500 p.s.i.a. The burning rates of both aluminized and nonaluminized composite propellants depended on acceleration. The effect of acceleration on burning rate depended on the burning rate of the propellant without acceleration, Al mass loading, and Al mass median particle size. The relative burning rate increase was greater for slow burning propellants than for faster burning propellants. The expnl results are compared to the analytical models proposed by Crowe for aluminized propellants and by Glick for nonaluminized propellants. The results indicate that these models do not adequately predict the observed relative burning rate increase with acceleration, and hence that more complex modeling will be required to explain the observed acceleration effect.

S.K. Sinha & W.D. Patwardhan, Explosivstoffe 16 (10), 223–25 (1968) & CA 70, 49144 (1969): The mechanism causing the plateau effect in the combustion of propellants with admixt of Pb compds (ie, the independence of pressure of the combustion rate in a certain range) is discussed. This effect is caused by the transport of free Pb alkyl radicals from the foam zone to the fizz zone, which decomp there, causing a more efficient combustion, and increase the temp of this zone by reaction with NO. An increase of pressure is assumed to displace the free radicals from this zone because of the increase of the collision rate; this leads to a decrease in the local temp, which compensates for the increased thermal conductivity. In a certain range, these two effects cancel, causing the plateau. At even higher pressures the radical mechanism becomes unimportant, so that the combustion rate increases again with pressure. The nonexistence of a plateau in very “hot” propellants is understood by this mechanism.

G.B. Northam, NASA Tech Note NASA-TN-D-4914 (1968) & CA 70, 49145 (1969). The combustion of aluminized solid propellants (polybutadiene-acrylic acid containing 70 wt% AP) was studied in the firing of unidirectional burning slab motors on a ballistics centrifuge. Acceleration levels were varied from 0 to 300g, and the acceleration load was directed normal into and out of the burning surface, as well as at orientations into the burning surface of 0°, 30°, 60° and 75°. The surface condition of each test sample after firing was examined by extinguishing methods. The average propellant burning rate, the surface pitting and the residues varied directly with the normal acceleration load into the burning surface. At orientations other than normal and into the burning surface, none of these factors showed much change thru the entire spectrum of acceleration levels. At the average chamber pressure of 500 p.s.i.a, the propellant burning rate increased about 21% over the range of acceleration levels. At the higher pressure levels, the propellant burning rate was most sensitive to increased acceleration loads. Empirical burning-rate equations are included, and it is concluded that ground-spin-test results should be extrapolated to flight performance with great care, and that changes in propellant formulations tending to reduce metallic fuel additive agglomeration would be effective in reducing the effects of acceleration level on combustion.

R.D. Gould, US Clearinghouse FedSciTechInform, AD-684244 (1968) & CA 71, 51808 (1969): The effect of variations in the composition of solid propellants on their tendency to show combustion instability at 1000 psi was studied using a T burner. AP particle size can have a large effect on the acoustic response and this is frequency-dependent. TiO2 is usually added to plastic propellants to promote stable combustion, and the mechanism of its action was detd. With a view to the potential use of O-balanced propellants, the effect of varying the oxidizer/fuel
ratio of plastic propulents was also studied.

E.W. Price, 12th IntSympComb (Proc) 14-20 Jul, 101-13 (1968) & CA 74, 89283 (1971): A review with discussion and 48 refs, stressing advances since 1964 in the understanding of oscillatory combustion. Price discusses the nature of the combustion zone and warns that generalizations from current knowledge, which pertain mostly to propulants with AP as oxidizer and rubber as binder, with AI as the metal if any, might not fit other types. The theory of combustion-flow interactions is outlined and the nature of the response function is discussed both in 1-dimensional, homogeneous flame models and in others proposed. Recent combustor stability analyses, esp those modeling low-frequency "nonacoustic" combustor instability, are mentioned. Of the techniques considered for exptl determination of the response function, two that had been used extensively are discussed: the T burner and the nonacoustic burner.

M.L. Bernard et al, CR AcadSci, Ser C, 272 (26), 2112-15 (1972) & CA 75, 101675 (1971): A generalization of the previously described (Bernard et al, 1971) ablation theory (for AP) combustion to include AP-based solid propulnts provides satisfactory fits to the exptl data of M. Summerfeld et al (1960), with reproduction of the two distinct pressure regimes observed in the combustion of AP-based powders between 0 and 100 bars. The solid binding agent is assumed to be easily pyrolyzable, with each mol producing several combustible gaseous mols, as in the case of pyrolytically degrading polymers.

N.E. Cohen, 13th Symp (Int) Combust (Proc) (1970), 1019-29 & CA 76, 61471 (1972): To analyze and explain the mechanism of combustion of powdered metals in contact with a solid oxidizer (AP) with the powdered metal dispersed in solid AP (I), the combustion of various compressed I-AI and I-Mg mixts in N₂ under various conditions in a high-pressure window bomb was studied. The regression-rate laws of the mixts at high and low pressures, the pressure limits for deflagration, and the structures of the combustion zone and of the surface were detd. The burning rate of various I-AI mixts, as a function of pressure, particle size, and mixt ratio was determined by cinemato-

graphy. The combustion was difficult to achieve under some conditions, and became less and less complete as the mass fraction of AI increased. Addition of 2% powdered Cu₂O as a catalyst markedly improved the ignition and combustion, raised the acceptable metal ratio from 25 to more than 50%, and markedly lowered the limiting combustion pressure. The combustion of I-Mg mixts was smooth below as well as above 1 atm, but with a different mechanism. In subatm combustion the pyrolysis surface melted but did not remain flat, and the Mg particles were harder to ignite. The regression rate of pressed I-Mg-2% Cu₂O samples rose with increase in Mg content; unlike the case with AI. The study of the molten and resolidified pyrolysis surface formed during subatm combustion of I-Mg mixts suggested a possible mechanism for the decompn of I.

A.M. Varney & W.C. Strahle, CombustSci-Techol 4 (5), 197-208 (1972) & CA 76, 61472 (1972): Expts were conducted on quench combustion of 2-dimensional propult sandwiches prepared with AP oxidizer and 4 conventional propult binders — polysulfide, polyurethane, polybutadiene acrylic acid, and carboxy-terminated polybutadiene. Propult sandwiches prepd with both single-crystal sheets and compacted polycryst sheets were burned and quenched at combustion-pressure levels from 300 to 2400psig for binder lamination thicknesses of 25-200μ. The quenched sandwich properties indicate that there is considerable interplay between the binder and oxidizer species on the oxidizer portion of the sandwich surface, primarily because of the ability of the binder to form a flowable melt prior to gasification; sandwiches prepared with all 4 fuels formed a surface melt during combustion at every pressure level. Mass flux data generated indicate that all 4 fuels were effective in increasing the AP deflagration rate in the high-pressure region where AP burning rate vs pressure curve has a negative slope.

M.W. Beckstead et al, 13 Symp (Int) Combustion (Proc) 1047-56 (1970) & CA 76, 61477 (1972): A model developed previously by the authors described the general combustion properties of 3 types of composite propulnts and of 2 oxidizers burning as mono-propulnts. The math limiting conditions of the model correspond to the combustion in various environments of 3 different oxidizers: AP, HMX, and KClO₄. The
3 composite propelants considered contained 78% of one of these oxidizers and 23% polyurethane binder by weight. The first case studied was that of a solid monopropellant burning with a single premixed flame; apparently AP and HMX burn with a considerable energy release at the burning surface and in the gas phase; both reactions must be considered. The second case was that of composite propelants containing KClO₄. These burn with a primary flame resulting from reaction of the oxidizer and binder decomp products. The third case was that of composite propelants, such as those containing HMX, which burn with a primary flame and a monopropellant flame, but no afterburning. Cases 2 and 3 are compared with calcns for a composite propellant containing AP. The combustion model was compared with exptl data for the burning rates, their dependence on particle size and concn, and on pressure and initial temp, and for the variation of surface temp and of pressure exponent with pressure. In all 3 cases, the model described the general combustion characteristics of the systems.

P.G. Willoughby et al, 13th Symp (Int) Combust (Proc), 1033–45 (1970) & CA 76, 61748 (1972): The photographic study of solid propelants burning in an acceleration environment supported previous findings that acceleration forces directed onto the burning surface may greatly raise the burning rate of aluminized solid propelants, probably by heat transfer to the solid below from the burning Al globules held on the surface. The burning of 6 different composite propelants at 200, 500 and 1000psia, and at accelerations ≤100g in a normal direction toward the burning surface, was photographed by high-speed color cinematoigraphy. Also, one propellant was photographed with the acceleration vector oriented at 75° to the surface. Pits were formed in the burning surfaces by the extra heat transferred from the burning globules. All of the aluminized propelants showed pit formation and growth, but the rate of growth depended on propellant compn, pressure, and acceleration level. A high-burning-rate propellant containing a Mg/Al alloy was not acceleration sensitive. The median diam of these agglomerates at 0 acceleration differed widely (130–440μ) for the different propelants. The diam increased with acceleration and with pressure drop. The propelants which formed the larger agglomerates were the most sensitive to acceleration. Scanning electron microscopy of residual slag and extinguished propellant surface showed the slag particles characterized by large numbers of small surface holes and by tubular voids in the interior. Photomicrographs of AP particles in extinguished propelants suggested subsurface evolution of gas and existence of a liq layer during combustion.

Ya.B. Zel’’dovich, FizGoreniyaVzryva 7 (4), 463–76 (1971) & CA 77, 64194 (1972): The influence of turbulence and nonturbulence is examined relative to a propellant burning in a gas flow. Equations indicate expnl methods for determining the magnitudes of the thermal conductivity and viscosity under turbulent flow, and permit a study of thermal flow distribution and temps in a gas wherein an exothermic chem reaction occurs. Equations for nonturbulent conditions can be used to calculate the distance from the surface of the propellant to the zone of intense chem reaction and establish the relation of bulk burning rate to the vol reaction rate. A discussion of the theory of erosion burning (wherein the flow of combustion products increases the rate of propellant burning) confirms the role of the Pobednostev criteria relative to such burnings.

V.F. Bul'dakov et al, FizAerodispersnykh-Sist, No 5, 77–82 (1971) & CA 77, 64195 (1972): The results of an expnl study of the burning of 2-component (finely ground oxidizer with a high-polymer compd or a ballistic propellant) heterogeneous systems under low pressure are presented. At a constant pressure, oscillatory burning was used.

Yu.A. Gostintsev et al, FizGoreniyaVzryva 7 (4), 476–82 (1971) & CA 77, 64917 (1972): Equations are given that indicate the changeover of the temp profile in the condensed phase of transition processes during propellant burning in a semiclosed vol, and give parameters relative to propellant and to surface, flame, and gas temps in the chamber. Graphic representations of intraballistic parameters as functions of time are given for four variants relative to such processes.

V.A. Strunin et al, FizGoreniyaVzryva 7 (4), 498–501 (1972) & CA 77, 64201 (1972): Equations relative to stationary burning stability indicate that such stability is greater at
lower activation energy for the chem reaction, and at higher heat of vaporization and initial temp. Instability is characteristic of substances which have a strong relation between rate and pressure. Stability criteria are significantly affected by the temp relation of the heat of vaporization.

C.M. Mihlfeld et al, AIAA J 10 (10), 1280–85 (1972) & CA 78, 6070 (1972): The response function relating mass flux perturbations of a burning solid propel is to externally imposed periodic thermal radiation was measured over a range of frequencies of 20–80, depending on the fuel binder, oxidizer loading, and propel transcucence. The compn and oxidizer loading affected the response, which is attributed to changes in the interfacial combustion dynamics. The total character of the response function is affected by changes in the propel fuel binder. A lower max response at resonace was noted for polybutadiene-acrylic acid-containing propels compared with polyurethane-containing opaque propels. Comparison of the measured response functions with predictions of theoretical models, which were modified to consider radiant-heat-flux effects for translucent propelants rather than pressure perturbations, suggest general agreement between theory and expt. The technique is suggested for study of the effects of propelnt formulation variations on solid-propel combustion dynamics.

D.W. Blair, CombustFlame 20 (1), 105–9 (1973) & CA 78, 113515 (1973): A simple heat-transfer model is coupled with an Arrhenius-type pyrolysis law to study the effect of solid-state heat-transfer losses on burning rates of solid rocket-propel strands. Such heat-transfer losses materially affect the burning rates and also cause extinction phenomena similar to some that had been observed exptly. Strand diam and compn, adiabatic burning rate, and the heat-transfer film coeff at the strand surface are important variables. Results of theoretical analysis are applied to AP-based composite solid propelnts.

R.A. Battista & L.H. Cavney, USNailTechInformServ, AD 753835 (1972) & CA 78, 161662 (1973): Solid rocket performance during rapid pressure increases differs greatly from predictions based on steady-state burning rate data. Rapid pressurization (150–250kpsi/sec) following a sudden throat-area decrease in

a "low L star" combustor produces pressure overshoots of 10% and burning-rate overshoots greater than 50%. A transient internal ballistics model was developed incorporating nonsteady continuity and energy equations for the chamber, nonsteady energy equation for the propelnt condensed phase, and a modified Zel'dovich heat feedback function for the propelnt, which, for the conditions considered, is known to burn in a thin quasi-steady reaction zone.

N.N. Bakhman, ArchProcesowSpalania 2 (1-2), 37–43 (1971) & CA 78, 99930 (1973): Flame propagation along a layer of solid oxidizable polymer or metal powder in contact with a layer of solid oxidizer was investigated. The oxidizer was compression molded into tubes made from the polymer or compressed on the surface of W or Al powder tablets. KClO₄, KClO₃, BaO₂ and KMN₄ were used as oxidizers. Poly (Me methacrylate) and polystyrene were the principal polymers used. For systems characterized by stable combustion, the flame-propagation rate was determined. The effects of the thicknesses of both layers, the density of the oxidizer layer, and the pressure on the flame-propagation rate were studied. The shape of the recess formed by combustion was compared with that resulting from the theory of diffusion.

O.Ya. Romanov & G.G. Shelukhin, GorenjeVzryv, MaterVsesSimp, 3rd, 94–9 (1971) & CA 78, 161665 (1973): A math analysis of the theory is presented on the basis of the combustion rate, the thermal conductivity, the heat capacity, the surface temp of the propelnt grains, and other factors. Expts were made to determine the relation of the combustion rate to acceleration for various propelnts. The rate of combustion at 70 atm was compared with the initial rate. The relation of the critical pressure of transitional laminar combustion to acceleration, and the dependence of the combustion rate of nitroglycerol to the pressure at various acceleration rates were determined. Expt observations were compared with results of theoretical calculs.

V.V. Kleimenov et al, GorenjeVzryv, MaterVsesSimp, 3rd, 426–28 (1971) & CA 78, 161666 (1973): Motion-picture and spectral studies of the combustion products from a model rocket engine were conducted to determine the progressive temps, to identify the combustion products, and to establish equilibrium condi-
tions in the system. The emission spectra in the visible and ultra violet regions of the combustion products of gunpowder N without and with addn of 5% Al were determined for incomplete (20–30 atm) and complete combustion (80–90 atm) regimes. Bands and lines of the following radicals and mols were identified in the continuous background of the emission spectrum of the combustion products: N₂, C₂, CO, CN, CH, OH, H₂O, and AlO, AlH, and Al in the case of the combustion of N-Al powder mxts. The electron temps for C₂, N₂, CN, and CO were 2200, 2000, 2210, and 1900°K resp. The differences between the measured progressive temps and the calc'd electron temps indicate the absence of thermodynamic equilibrium.

N. Ryan & A.D. Baer, USNatTechInformServ, AD 757234 (1973) & CA 79, 33259 (1973): Conclusions of previous publications re combustion transients of solid propels are re-stated. The area of studies reported are an evaluation of the hot wire-ignition method for characterizing propels; development and study of gas-fueled analog of the solid-propel T-burner low-frequency combustion; high-frequency acoustic instability of solid propels, the T-burner and the radial-mode, radial-flow burner being used with the same propel systems; development and evaluation of a technique for measuring the solid-propel response function to external energy perturbations at the burning surfaces; measurement and evaluation of transient temps of propel flames during rapid depressurization; and low-pressure combustion of several different solid propels, including their low-pressure deflagration limits, the elec conductivity near the surface, the extinction requirements, and spontaneous reignition.

R.F. McAlevy, III & R.B. Cole, USNatTechInformServ, AD 757066 (1973) & CA 79, 33260 (1973): Investigations over an 11-yr period of the mechanism of composite solid-propel deflagration and its component processes are reviewed. Exptl studies and techniques involving diagnostic measurement on analog burners of several types and characterizations of the linear pyrolysis of propel ingredients (polymers and AP) are included along with efforts to model the overall mechanism. All publications resulting from the work reported are cited.

N.N. Bakhman et al, CombustFlame 22 (1), 77–87 (1974) & CA 80, 110502 (1974): AP, KClO₄, formamidine perchlorate (I) and tetramethylammonium perchlorate (II) were used as oxidizers and poly (Me methacrylate) (III), polystyrene, soot, S and guanidine nitrate were used as fuels. For AP-III mxts, the catalyst effectiveness, Z = u/u₀ (where u₀ is the burning rate of an uncatalyzed mixt) increases with pressure. The Z for AP-III and AP-polystyrene mxts decreased with increasing ambient temp. Rapid increases in u and A occurred at small catalyst content but at m_c = 1–5%, Z increased only slightly. The catalyst effectiveness decreased as the u₀ increased; Z_max = A/u₀₀^0.65, in which A is a constant. AP- and I-based mxts were much more sensitive to catalysis by Fe₂O₃ than KClO₄ and II-based mxts, but Fe₂O₃ was an excellent catalyst for II when u₀ was decreased by adding diluents (KCl, NH₄Cl, or Al₂O₃). A diffusion-controlled model is proposed, taking into account the competition of catalytic and homogeneous reactions. The mechanism of catalysis in the burning zone is discussed.

H.C. Mongia & L.L. Ambs, CombustFlame 22 (1), 59–69 (1974) & CA 80, 110503 (1974): Some results are reported of the study of transient burning rate and crit-pressure decay rate required to cause extinction of a steadily burning solid propel subject to sudden depressurization. It is possible that the solid decomp products are rich in oxidizer immediately after the beginning of depressurization and rich in fuel afterwards. The calc'd transient burning rates agree qualitatively with exptl values reported by Norton and Schulz (1970), Yin & Hermance (1971) and Fletcher & Bunde (1965). A stability analysis using the linear approximation predicts the existence of a min burning-surface temp below which stable combustion of the solid propel is not possible. The analysis correctly predicts the crit depressurization rate required to extinguish a burning solid propel by sudden venting of the combustion chambers.

N.S. Cohen et al, AIAA J 12 (2), 212–18 (1974) & CA 80, 135471 (1974): The effects of inert polymer binder properties on composite solid propel burning rate are described. Surface pyrolysis data for many polymers over a wide range of conditions are used to derive kinetics constants from Arrhenius plots and heat of
decompn from an energy balance. Pyrolysis kinetics varied between the polymers, but were found to be independent of N pressure, the presence of AP or catalysts in the sample, and their combinations. All of the polymers exhibited molten, boiling surfaces mingled with char, to varying degrees; the low activation energies may be associated with the boiling or with a weak-link decompn mechanism. Relevant data were input into the Derr-Beckstead-Price combustion model in order to associate binder properties with known effects on burning rate in simple propellants. Although the effects were predictable, they stemmed from properties other than pyrolysis kinetics. The role of the binder appears to be in controlling the gas phase processes and not the surface pyrolysis properties.


K.K. Kuo & M. Summerfield, AIAA J 12 (1), 49–56 (1974) & CA 80, 135475 (1974): High-speed flame propagation well above the normal deflagration rate is achieved in the combustion of porous propmts. Gas-penetrative burning of porous propmts under strong confinement is inherently self-accelerating, but under suitable physical conditions, a constant-speed combustion wave can be produced. The jump conditions and the equiv Rankine-Hugoniot (R-H) relation for porous proplnt burning are derived. Whereas the usual R-H relation forbids the existence of a steady-state combustion wave that has both a pressure rise and a density decrease (called forbidden region on the R-H curve), this restriction can be bypassed here and high-speed compressive-expansive waves are legitimate solutions of the equations. The structure of the wave and its speed of propagation are affected by propmt porosity, ignition temp, specific burning area, gas permeability and pressure. The flame propagation speed is determined as the eigenvalue of this 2-point boundary value problem.

Reactivity

M. Frey, Explosivstoffe 15 (5), 97–105 (1967) & CA 68, 31678 (1968): The decompn of Ph₃NH in NG and NC was measured at 50–100°C. At 90°C, samples open to the air decomp more rapidly initially, but more slowly later, and partially closed samples reached an autocatalytic stage in 18 days, whereas closed samples decomped more slowly at first, but continued to decomp and took longer to reach the autocatalytic stage. The disappearance of Ph₃NH was followed by extraction with CH₂Cl₂, drying the extract, dissolving in MeOH, and measuring polarographically. Nitro and nitroso diphenylamine could be measured directly. The 2-nitro and 4-nitro derivatives could be separated by thin-layer chromatography. Residual Ph₃NH could be determined after conversion to the N-nitroso derivative. The Ph₃NH decreased linearly with time at a rate set by the decompn of the NG or NC. The N-nitrosodiphenylamine passed thru a max and the nitrodiphenylamine increased regularly. Based on these data, the energy of activation for the decompn of NC was found to be 29.5kcal/mole with a range of 27.2–34.2 kcal/mole for different samples. Similar calcs from the stability times yielded values of 27.2–27.6kcal/mole. This compares with the literature values for pure NC of 39.2 and 49kcal/mole. Similar exps with NG indicated an energy of activation for decomp of 29kcal/mole. It is suggested that these values can be used to estimate the life of the compns under normal storage temps.

G.D. Sammons, Analytic Calorimetry, Proc. AmerChemSymp, 155th, 305–11, Edited by Porter, Plenum Press, NY (1968) & CA 70, 89323 (1969): The propmts studied were in the form of disks, 3–5mm in diam and 280–840µ thick. A modification of the Rogers & Morris equation (of CA 64, 17345) based on the theory of Borchardt & Daniels (of CA 51, 6296) was used in evaluating the kinetic parameters. The thermogram of the propmt binder (a linear polybutadiene polymer) shows an exotherm at 570°C (probably due to vinyl polymerization). The average activation energy was 33 ± 3kcal/mole. The thermogram of AP (oxidizer) shows a phase change at 516°C (orthorhombic to cubic), a low temp decomp at about 600°C (30%) and a high temp decomp (100%) at 725°C.

The termination at 30% decomp at 516°C is
probably due to a concn of adsorbed ammonia on the surface of the AP. The activation energy for high-temp decompn (127 kcal/mole) is in disagreement with that obtained by thermogravimetric analysis (35 kcal/mole) and is due to the fact that differential scanning calorimetry is sensitive to many other processes, such as proton transfer, taking place in the sample to which thermogravimetric analysis is not sensitive.

H. Selzer, AGARD Conf Proc 52, 24 (1970) & CA 73, 100599 (1970): AP-based composite solid propulnts, most commonly used in modern day rocketry, are discussed. Recent work since previous reviews is discussed and areas where additional work is needed are indicated. New facts are given concerning the effects of lattice defects and condensed-phase behavior of the burning process. The findings require revision of the theoretical models to account for lattice defects, for a change from fast to slow decompn, and for spots of high reactivity (size 1–10 μ)

J.F. Lieberherr, AGARD Conf Proc 52, 23 (1970) & CA 73, 100605 (1970): In hybrid-propellant combustion studies, disparities between expnl results and simplified models based on gas-solid heat transfer led to research on other mechanisms. New models, mathematically derived, based on chemical surface reactions are in better agreement with actual results. The surface reactions are less related to simple vaporization than to a melting mechanism, followed by liq flow. The melting rate depends on the gasification rate and has an inverse pressure sensitivity, while the gasification rate has a direct pressure sensitivity. It was concluded that means that will destroy the liq layer and promote combustion efficiency, other than already existing turbulators, are difficult to visualize. One possible way is to make use, as much as possible, of surface reactions and to avoid propulnts that have too low a Prandtl number in the liq phase. Another way would be to take advantage of the particular conditions under which combustion takes place in the injection zone.

G.L. Pellett, AIAA J 8(9), 1560–66 (1970) & CA 73, 100610 (1970): A pulsed ruby laser-mass spectrometry technique was developed and applied, wherein granular mixts of AP and light-absorbing substrate materials were rapidly flash-pyrolyzed (0.8 msec) within the low-pressure ion-source chamber of a Bendix TOF mass spectrometer. Gaseous products from AP mixed with carbon black, Cu chromite, Fe₂O₃, and MnO₂ indicated a predominance of high-temp heterogeneous reactions. The first step appeared to be proton transfer dissociation of AP into NH₃ and HClO₄. Adsorbed HClO₄ underwent rapid heterogeneous decompn on the substrate material; Cl₂O and HCl were evolved as major products, but ClO₃, ClO, and Cl₂ were only minor products. Chemisorbed O and O carriers, such as OH and ClO were likely formed on the substrate simultaneously, however. These could react with adsorbed NH₃ and its dehydrogenated fragments to form H₂O, NO, and HOCl as major gaseous products. N₂, N₂O, and NO₂ were minor products. Low-pressure isothermal decompns of AP and AP/substrate mixts in a glass capillary were utilized to compare product distributions. The site of HClO₄ decompn (crystal vs substrate surface) was at least as important as temp and effective residence time in determining the predominant chemistry.

K.O. Hartman & R.C. Musso, WestStResSect-CombustInst (Pap) WSCI 72–30 (1972) & CA 78, 113507 (1970): The thermal-decompn kinetics of liq NG dispersed in alkali metal halide disks in the range 90–160°C is first order; K = 2.5 x 10¹⁴ exp(–34,400K/1500 الهند) sec⁻¹. The rate determining step is probably scission O–N bonds. In the liq phase, the decompn mechanism is more complex with an overall rate of 0.5 order. The thermal decompns of EtNO₃ and ethylene dinitrate in halide disks were also studied. The increase in rate from EtNO₃ thru ethylene dinitrate to NG is attributed to an increase in the entropy of activation. Thermal decomp of CMDB propulnts containing AP shows autocatalytic behavior; for prolonged storage, a stabilizer is necessary. The rate-controlling process during the induction period is probably decompn of NG. CMDB propulnts containing AP should last 50 years without significant degradation at 40°C when stabilized with resorcinol.

A.N. Kiselev et al, FizGoreniyaVzryva 8(4), 595 (1972) & CA 78, 161672 (1973): The effects of shock waves produced by Ammonite 6Z expl in powdered AP were examined. The AP, after having been exposed to explin, was studied by DTA (differential thermal analy-
sis) and TGA (thermogravimetric analysis). Although no chemical changes occurred, there was a considerable change in the density of the dislocations, resulting in an increasing number of pores. These changes strongly affect the temp of the beginning of low-temp thermal decmpn. The rate of high-temp decmpn is not influenced by the shock-wave pretreatment.

**Detonability & Safety**

R. McGill, USDeptCom, Office Tech Serv, AD 272424 (1961) & CA 60, 10463 (1964): Exps, propelnts and pyrotechnic safety covering laboratory, pilot plant, and production operation

W.H. Anderson & R.F. Chaiken, ARS (Amer Rocket Soc) J, 31 (10), 1379–87 (1961) & CA 61, 6849 (1964): A theoretical model of propagation of detonation in propelnts is presented. This model is based on the hypothesis that detonation is propagated by the same rate-controlling chemical reactions that occur during normal burning of the propelnt. In particular, it is assumed that a grain burning of the oxidizer occurs and that the rate of linear-surface decmpn (pyrolysis) of the oxidizer can be used to describe the rate of the detonation reaction. Kinetic data on the surface decmpn of AP, which were obtained by the hot plate-linear pyrolysis technique, suggest that sublimation of AP (with an apparent activation energy of about 22 kcal/mole) is the rate-controlling step in the surface decmpn of this oxidizer. A discussion is presented on how these data can be used in conjunction with the detonation model to calculate the min (crit) diam at which detonation can propagate in a cylindrical charge of solid propelnt. The possible effect of various propelnt parameters, ie, oxidizer-binder ratio, oxidizer particle size, and confinement on the detonation process is discussed. The role of ignition, diffusion, and heat conduction processes in the detonation and rapid deflagration of solid composite propelnts is discussed. A preliminary theoretical approach to accelerating burning in porous propelnt is also presented. This approach indicates that porous burning in rocket motors containing solid composite propelnts can lead to very rapid chamber pressure build-up so that an exph could occur within several millisec after porous burning begins.

Donna Price et al, IndChimBelge 32 (SpecNo), 506–10 (1967) & CA 70, 49142 (1969): Solid rocket propelnts were tested for shock sensitivity and detonability by the NOL Standard Card-Gap Test. The propelnts act as high explosives, showing the same trends as conventional explosives of increasing shock sensitivity with increasing porosity or increasing temp. A porosity effect and a temp effect upon detonability were also observed. Some relatively low energy materials are improperly classified as insensitive.

H.M. Shuey, AdvanChemSer No 88, 296–300 (1969) & CA 71, 51811 (1969): The identification and evaluation of hazards in the manuf of solid propelnts are being brought to a semiquantitative state of the art. Indiscriminate use of routine "approved" tests is being supplanted by analysis of the processes and operations to be used. By identifying the principal stresses involved (as thermal, friction, impact, electrostatic), one can design specific "use" tests resulting in numerical values broad enough to distinguish discrete differences in stimuli necessary to ignite materials tested. Consideration of the consequences of such ignition allows tests to assess the worst catastrophe probable and suggests modifications of process conditions or plant construction to minimize risk to personnel, facilities, and product.

N.J. Blay & I. Dunstan, USNatTechInform-Serv, AD 744871 (1970) & CA 78, 6069 (1973): Compatibility and stability problems encountered in the design and development of weapon systems containing exps and solid propelnts are discussed. Safety during storage and reliability in service are emphasized. The effects of materials used near or in contact with the exps and propelnts are considered.

**Analytical Procedures & Data**

M. Roth, USDeptCom, Office TechServ, AD 296018 (1963) & CA 60, 10464 (1964): In general, stabilizers function by reaction with propelnt decompn products. A number of methods have been described and a preliminary evaluation of these methods was conducted by several labs under a cooperative program. Based on results from these screening tests, the PicArsn spectrophotometric methods for available stabilizer and primary degradation products were selected for further study. The initial phase of this program was an attempt to standardize the necessary spectrophotometric factors. Significant differences with regard to the factors obtained
existed between labs. It was suggested, however, that these differences would be cancelled if each lab used the factor appropriate to its spectrophotometer.

G.N. Kruse et al, USDA/Com, Office Tech-Serv, AD 297335 (1959) & CA 60, 10464 (1964): Solid-propellant combustion products resulting from firing 2.5-inch rockets from F-102 airplanes were found to consist of C, various organic materials, and Mg or MgO. Twenty-nine materials were tested to determine their efficiency in removing heavy combustion-product deposits. Three of these materials, Rocket Cleaners X2-6, X2-9 and X2-11, were suitable for combustion-product removal.

W. Stark & B. Hornstein, NASA Doc N62-12792 (1962) & CA 60, 10464 (1964): A spectroscopic method for measuring burning rates in an operating solid propellant motor was investigated. The principle is to detect spectroscopically in the exhaust the appearance of emission from a tracer compd previously embedded in the grain. Li tracer emission was detected against background radiation from Al2O3 in the exhaust. The necessary correlation between tracer detection in the exhaust and progress of the burning surface in the motor was partially accomplished; difficulties encountered relate primarily to tracer excitation by the flame front.

S.K. Sinha et al, Current Sci (India) 33 (5), 141–2 (1964) & CA 60, 11835 (1964): The thin-layer technique (CA 60, 6691) utilizes aliquots of propelnt ether extract (I) and the ether soln (II) of a known mix. II consists of nitrates of glycerol and glycol, di-Bu or di-Et phthalates, Et or Me centralites, DNT, and diphenylamine. The chromatoplates are made of 85:15 silica gel and plaster of Paris. These plates, containing spots of I and II, are developed with 1:1 C6H6/petroleum ether, then sprayed with specific detectors by color. The method is much quicker and easier than chemical analysis and simpler than infrared spectroscopy and column chromatography.

J. Tranchant, IndChimBelge 32 (Spec No), 601–5 (1967) & CA 70, 49146 (1969): A gas-phase method of chromatographic analysis is described for measuring stabilizers and some of their derivatives, as well as a method for the chromatographic sepn in thin layers of nitro and nitroso derivatives, as well as an accurate detn of mixts of Ph2NH and centralite. With thin-layer chromatography, the gas-phase chromatographic method is a good method for studying the stability of powders during storage.

F.I.H. Tunstall, Chromatographia, 11–12, 477–80 (1968) & CA 70, 41947 (1969): A knowledge of the nature and amount of gas evolved from stored propelnt compts provides valuable information on the stability, compatibility, handling and storage characteristics of such compnts. A gas chromatographic method is described for the sepn and detn of N, O, CO, NO, CO2 and N2O employing a single column thermal conductivity detector system. Sepn of N, O, CO and NO is achieved by operation of a 4.5 m column packed with Porapak Q at –70°C and by rapid heating of the column to +20°C. CO2 and N2O well separated, are eluted. For detection, calibration curves of gas partial pressure against integrated peak area were produced.

K. Mehlhose, Explosivstoffe 20 (3-4), 37–70 (1972) & CA 78, 113513 (1973): Methods developed for detn of H2O in gun and rocket propelnts are: column distn with n-ProH and gas-chromatographic analysis of the distillate, corrected for continuous formation of water in decompn reactions; and photometric methods, both based on the reaction of CoCl2 with water. Choice of the methods is based on a critical review (117 refs) of the usual methods of water detn by chemical and physical methods. A theoretical and expmt analysis of the new methods was made and their results compared with those of older methods. Application to mono-, di-, and tribasic and to double-base NC and poly (vinyl nitrate) propelnts is discussed.

Miscellaneous

R.L. Bohon, AnalChim Acta 35 (12), 1845–52 (1963) & CA 60, 1527 (1964): Approx heats of expln, Qv, were detd on mg amounts of propelnts and expls by differential thermal analysis (DTA). Small-screw-cap metal cups sealed with a Cu washer served as constant vol sample containers; the initial cup pressure could be controlled from 0 to approximately 1000 psia. The calibration constant was calc'd for each run from the total heat capacity of the cup and the relaxation curve, thereby compensating for equipment variations.
Nine runs on JPN propellant gave an average $Q_v$ of $1100 \pm 140 cal/g$ at $250^\circ$. Systems examined included N-5, JPN, ABL-2056, TNT/AN/NaCl, TNT/AN/paraffin, and C(NO$_2$)$_4$ propellants; TNT, RDX, PETN, Tetryl, and NG expls. DTA-detd $Q_v$ values can be misleadingly low when evaluating the potential destructive power of a material.

R.C. Oliver et al., USDentCom, Office TechServ, AD 265822 (1961) & CA 60, 10466 (1969): Metal additives for solid propellants: formulas for calculating specific impulse and other propellant performance parameters are given. A mathematical treatment of the free-energy minimization procedure for equilibrium compn calcs is provided. The treatment is extended to include ionized species and mixing of condensed phases. Sources and techniques for thermodynamic-property calcs are also discussed.

E. Kuletz & J.M. Pakulak, Jr, USDentCom, Office TechServ AD 291792 (1962) & CA 60, 10466 (1969): Effects of thermal aging on a cast-composite propellant: the activation energy, $E$, frequency factor, $A$, and specific rate constant, $k$, were determined for the exposed surface, subsurface, and internal regions of 5 cast-composite propellants (ANP-2639 AF) motors thermally aged at various temps from $95^\circ$ to $165^\circ$F for different periods. The $E$ values of the exposed surfaces for the $95^\circ$ and $130^\circ$-aged samples were essentially identical (23kcal/mole), while there was a 4kcal/mole increase for the aged samples at $150^\circ$ and $165^\circ$F. For the subsurface regions, 0.005-0.010 inch below the surface, the $E$ values are similar — each is approximately 25kcal/mole. $E$, as well as $A$, varies with the aging history of the sample. A comparison of all $E$ values and a study of the relations of temp to a rate factor indicate that, for the thermally aged propellant grains, the primary component altered at the surface is the binder. In the interior, it is the oxidizer.

J.W. Jones, APL Bull Meeting, Interagency Chem Rocket Propulsion Group, Working Group Mech Behavior, 3rd, 1, 371-94 (1964) & CA 63, 17781 (1965): Propellant failure characteristics were measured in uniaxial and biaxial stress states for polybutadiene acrylic acid and Nitroplastisol propellants, and failure conditions were examined over a wide range of temps. The observed failure conditions were compared for various failure criteria, and it was found that a max tensile stress criterion accurately resolved the data for uniaxial tensile, biaxial tension-tension, simple shear, and biaxial tension-compression stress states. The expls gave indications of the granular reactions of the solids during deformations to failure in tests made in the biaxial tension-compression mode. Examination of the influence of temp on the multiaxial failure characteristics of propellants gave evidence to support the applicability of the max stress failure criterion over wide ranges of temps. In studies of the effect of binder and oxidizer variations on failure, it was found that reasonable agreement with the max tensile stress criterion was obtained for wide variations in formulations.

D.E. Cantey, APL Bull Meeting, Interagency Chem Rocket Propulsion Group, Working Group Mech Behavior, 3rd, 1, 317-44 (1964) & CA 63, 17782 (1965): Dielectric spectroscopy was investigated as an analytical tool to assist in the elucidation of chemophysical effects in solid propellant systems. Complex dielectric properties were measured over a wide temp range and at frequencies from 50 to $10^5$ cycles/sec for polybutadiene-acrylic acid (PBAA), carboxy-terminated polybutadiene (CTPB), and NC-base propellants and ingredients. The measurement range was extended to low frequencies by measurement of dielectric absorption response to step function dc potentials over time ranges from 10 to $10^6$ secs. Spectral response of the complex dielectric constant storage and loss components is interpreted in terms of classical electrical polarization mechanisms.

J.N. Lhuillier, Ind Chim Belge 32 (Spec No Pt 3), 669-75 (1967) & CA 70, 69708 (1969): A discussion with 10 refs of combustion instability in solid-propellant rocket engines. Two different types of instability are considered: acoustic and non-acoustic instability.

P. Tavernier, Ind Chim Belge 32 (Spec No Pt 3), 337-46 (1967) & CA 70, 69709 (1969): A discussion with 14 refs on expls and propellants considering the thermodynamic characteristics of expl substances, the kinetics of combustion of powders and the effects of catalysts, corrosion, and instability on the kinetics, the occurrence of deflagration on detonation, and forms of solid mixts in view of the augmentation of their performance and the extension of conditions used in their mixts. The importance of modern methods of calcn is stressed.
G.A. Fluke, AdvanChemSer No 88, 165–87 (1969) & CA 71, 51809 (1969): The processing techniques for manuf of composite solid propulsions are described. The general operations of oxidizer prep, binder and fuel prep, propellant mixing, and chamber insulation and lining are illustrated by typical flow charts and descriptions of the equipment used. Limited data on the performance of this equipment are presented. The importance of characterizing the processability of propellants is introduced together with an instrumental method for achieving this characterization on a comparative basis. New processing systems, such as pneumatic mixing and inert diluent mixing, are discussed with their apparent advantages and likely limitations.

A.E. Oberth & R.S. Brenner, AdvanChemSer, No 88, 84–121 (1969) & CA 71, 51810 (1969): Solid propellant technology as pertaining to polyurethane-based propellants is presented. Particular emphasis is placed on the newer developments as well as the fundamental knowledge gained in the field. Much of this knowledge is not restricted to solid propellant technology but is of general nature. This includes contributions to kinetics and mechanism of the urethane reaction, metal catalysis, the effect of fillers on mechanical properties of filled elastomers, tear phenomena in composite materials, the importance of the interface between solid particle and matrix on physical properties, and the mechanism of filler reinforcement. Progress pertaining more directly to propellant technology includes such topics as catalyst modification to increase the pot life of propellant batches, calcn of mix viscosities of multinodal dispersions, mechanism and prevention of moisture embrittlement, and others.

D.W. Blair & W. Lake, AIAA J 7 (9), 1808–10 (1969) & CA 71, 126690 (1969): The radiant energy flux emitted thru a small viewing port in the side of an internal burning cylindrical solid propellant rocket motor is detd, and the data are interpreted in terms of net heat flux to the burning surface, ie, in terms of heat transfer from the gas phase flame zone to the solid surface to provide the enthalpy of heating and vaporization for the solid phase. Data are given for solid fuels comprising AP in a polybutadiene-acrylic acid or polyurethane binder. The radiant energy flux is apparently a significant portion of the total heat flux at the burning surface of the solid propellant.

K. Suzuki et al, KogyoKayaku 30 (3), 126–30 (1969) & CA 71, 126692 (1969): Composite propellants composed of AP 65–80, Al 7–8, binder (polybutadiene, polyether, polysulfide) 14–28; and burning catalyst 1–3% by wt were subjected to the following aging test: outdoors, in dry N at ambient temp and 80°; with wetting at 50°, and 30% relative humidity for 12 days, and drying with CaCl₂ at 3mm. In summer, the elongation and tensile strength of polysulfide and polybutadiene-based propellants decrease in outdoor air. In winter, and even in summer, the properties are restored by drying. Propellants using polyester as binder absorb considerable moisture and depolymerization occurs. No change in mechanical properties is observed in polybutadiene propellants at ambient temp in dry air, but at 80° a slight change is observed. Polybutadiene propellants absorb moisture and an increase in elongation and a decrease in tensile strength occur at higher humidity, but these properties are restored by drying.

T.L. Boggs et al, AIAA J 8 (2), 370–72 (1970) & CA 72, 113371 (1970): Scanning electron microscopy is used to study the surface structure of solid propellants, propellants prepared from AP (I) and polyurethane or carboxylated polybutadiene. Polyurethane propellants are self-extinguishing at high pressure due to the flow of molten binder over I crystals. I crystals formed a thin surface melt with gas liberation in the molten phase.

V.A. Veretennikov et al, FizGoreniyaVzryva 5 (4), 499 (1969) & CA 72, 123552 (1970): Shock compressibility of compact and porous NB (Ballistite) propellants: Shock Hugoniots of 60/40 NC/NG were determined at ρ = 1.63 and 1.0g/cc, respectively. Particle velocity, u, was measured:

\[ U = 1.70 + 1.85u \text{ for } \rho = 1.63 \text{g/cc} \]
\[ U = 0.58 + 1.68u \text{ for } \rho = 1.0 \text{g/cc} \]

ΔT at shock front is calc'd.

V.V. Aleksandrov & S.S. Khlebnii, FizGoreniyaVzryva 6 (4), 438–43 (1970) & CA 75, 89714 (1971): Earlier work showed that the surface temp, Tₜ, of NG powder (a mixt of NC, NG and DNT) in flameless combustion does not depend on the initial temp. On the basis of expts conducted at elevated temps and pressures, the mean heat of vaporization of a volatile com-
ponent was estimated to be about 26kcal/mole, and a formula was derived for the relation between the pressure \( p \) and \( T_s \) on the assumption that vaporization of these components determines \( T_s \). \( T_s \) at \( p \) less than 20–30mm cale is from this formula was less than 194–98° vs 300–10° determined exptly. NG propiql tablets were heated in a vacuum. Surface temps were measured and related to diffusion of the volatile components to the surface followed by their evaporation. They indicated that, upon evaporation of NG and DNT, a surface must form that consists almost entirely of NC and that this surface becomes overloaded to a temp above the bp of the volatile components. Calculation showed that if flameless combustion of NG propiql took place at a \( T_s \) equal to the bp of the volatile components (about 200–30°), the combustion rate would be lower by a factor of 18–50 than that observed exptly.

A. Sapinski, Arch Procesow Spalania 3 (2), 179–90 (1972) & CA 78 99929 (1973): Temp measurement of a flame containing solid particles by the emission-absorption method: The method was used for investigation of solid propiql containing Al and Mg powder. The method is described in detail and its errors are analyzed. The effects of solid particles on radiation propagation are discussed.

H. Schubert, ChemZtg 97 (9), 486–92 (1973) & CA 80, 28964 (1974): A brief historical survey of solid rocket propiqls is followed by a description of solid propiql motors and of the uses of the propiqls. The compn and the process technology of two fundamentally different types of propiqls, ie, homogeneous or double-base solid propiqls and heterogeneous or composite solid propiqls, are described. Their properties are reviewed.

Written by J. ROTH & E. L. CAPENER

Refs: 1) C.F. Schönbein, SitzungsberNaturforschgesBasel 7, 27 (1846) 2) J.H. Pelouze, CR 23, 809, 837, 861, 892 (1846) 3) E. Schulze, DeutschenIndustrie-Ztg 10, III (1865) 4) F. Volkmann, AustrianP 21/208, 21/257 (1871); also according to O. Guttmann, “Zwanzig Jahre Forschritte in Explosivstoffen”, Berlin (1909); & SS 4, 16 (1909) 5) J. Hartig, “Untersuchungen über den Bestand und die Wirkungen der explosiven Baumwolle”, Braun-
CA 73a) J.P. Flynn et al, USP 3865659 (1975); not found in CA 74) P.L. Nickols Jr, USP 3870578 (1975); not found in CA 75) J.B. Eldridge et al, USP 3876477 (1975); not found in CA 76) J.W. Lavitt, USP 3890175 (1975); not found in CA 77) D.C. Sayles, USP 3914141 (1975); not found in CA 78) C.W. Huskins, USP 3914140 (1975); not found in CA 79) M.L. Jones & D.W. Booth, USP 3914139 (1975); not found in CA 80) D.C. Sayles, USP 3914142 (1975); not found in CA 81) R. Lantz, USP 3923564 (1975); not found in CA 82) D.C. Sayles, USP 3932241 (1976); not found in CA 83) D.A. Madden, USP 3933543 (1976); not found in CA

Propene and Derivatives


3-Azido-1-Propene. See under “Allylazide” in Vol 1, A137-L

1,3-Diazidopropene-(1) (Bistriazopropylene or α, γ-Diazidopropylene). N₃.CH₂.CH.CH₃, mw 124.13; N 67.72%; yel liq; bp 78-79° at 26mm; d 1.1572g/cc at 25/4°; RI 1.5202. Volatile in steam. Prepn is by shaking an alc soln of 2-chlor-1,3-diazidopropene with a concd aq soln of K hydroxide for three hrs. The compd is a v sens high expl

Diazopropene (Diazopropylene or Vinyldiazo-methane). See under this title in Vol 5, D1173-L

Aminopropenes and Derivatives. See in Vol 1, A253-R to A254-L

Nitropropene Polymers. There are two nitropropenes which can be considered energetic materials, 1- and 2-nitropropene polymers

1-Nitropropene-(1) Polymer

Monomer

(Cis- or trans-) 1-Nitropropene-(1) (α-Nitropropene). CH₃.CH:N.O₂; mw 87.09; N 16.09%; OB to CO₂ = -119.42%; the cis form is v unstable, hence all measurements are of the trans isomer; mobile, pungent colored liq; bp 37° at 10mm; d 1.0661g/cc at 20/4°; RI 1.4527, 1.4545, 1.4559 (sep measurements). Soln in Na acetate soln, ethanol and hexane. Prepn is by boiling an ethereal soln of β-nitro isopropyl acetate and K bicarbonate and then recovering the prod by shaking with eth. The trans monomer is unaffected by ambient storage for one year and will not react with w (Ref 3)

Polymer

1-Nitropropene-(1) Polymer.

\[
\begin{array}{c}
\text{H} \\
\text{O₂N·C} \\
\text{H·C} \\
\text{CH₃}
\end{array}
\]

n; yel brn, odiferous powd; bp, decompn. Sol in hot glacial acetic acid and NaOH; insol in w and most org solvents. Polymerization occurs vigorously on treatment with an alkali such as aq K bicarbonate

2-Nitropropene-(1) Polymer

Monomer

2-Nitropropene-(1). CH₃.C(NO₂):CH₂; mw 87.09; N 16.09%; OB to CO₂ = -119.42%; yel liq, strong lachrymatory properties; rapidly turns grn and decomps to a black tar on being
kept in the dark for several days; bp 48–49° at 59.5 mm, vigorous decomp at 100° and ambient press; d 1.0492 g/cc at 20/20°; RI 1.4292 & 1.4296 (sep values). Sol in eth. Prepn is by pyrolysis of 2-nitropropylene yl and 200° without melting. Sol in acet, dioxane and acetic anhydride. Prepn of the polymer by vigorous stirring of the monomer with a satd aq soln of K bicarbonate. The crude prod is purified by w washing and air drying. The yield is 93.2%.


3-Nitropropene (1) (γ-Nitropropylene or Nitroallyl). O₂N₂CH₂.CH₂; mw 87.09; N 16.09%; OB to CO₂ –119.42%; color liq with a sharp bitter odor; bp 125–30°; d 1.051 g/cc at 21°; RI 1.4270. Sol in ethanol and eth; insol in w; volatile in hot eth. Prepn is by reacting for three-quarters of an hour at 40°, a mixt of Ag nitrate and sand with 10g of allyl iodide dissolved in three times its vol of eth

The sodium salt, Na₂C₆H₄O₂N₂, which is v sol in w and sol in ethanol and ether, expls with great brilliance at 200°.

Ref: Beil 1, 203 & (764)

Propenenitrile. See under “Acrylonitrile” in Vol 1, A97-R

3-Bromopropene (1) (γ-Bromopropylene or Allyl bromide). CH₂Br.CH₂.CH₂; mw 120.98; liq; mp –119.4°, bp 70° at 753mm; d 1.398 g/cc at 20/4°; RI 1.4697. V sol in ethanol and eth; sol in chlf, carbon disulfide and carbon tetrachloride; insol in w. Prepn is by reacting a 3 molar soln of aq bromic acid (48%) with 1 mole of allyl acetate at RT; yield is 100%. Expl limits (in air) are 4.4–7.3%; flash pt is –1°.

Ref: 1) Beil 1, 201, (84), (711) & (753) 2) Bretherick (1975), 355

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Color &amp; State</th>
<th>mp, °</th>
<th>bp, °</th>
<th>d, g/cc at 20/4°</th>
<th>RI</th>
<th>Soluble in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis</td>
<td>liq</td>
<td>–134.8</td>
<td>32.8</td>
<td>0.9347 at 20/4°</td>
<td>1.4061</td>
<td>eth, acetone, benz; chlf</td>
</tr>
<tr>
<td>trans</td>
<td>liq</td>
<td>–99</td>
<td>37.4</td>
<td>0.9350 at 20/4°</td>
<td>1.4058</td>
<td>eth, acetone, benz; chlf</td>
</tr>
</tbody>
</table>
Prepn of the cis isomer is by boiling cis-1,3-dichloropropene-(1) with LiAlH₄ in diisopropyl ether. The trans isomer is similarly prepd using trans-1,3-dichloropropene-(1). Expl limits in air are 4.5 to 16%, and the flash pt is -6° for both isomers.

Refs: 1) Beil 1, (697) & (737) 2) ChemRubHdb (1975), C457 3) Bretherick (1975), 355

2-Chloropropene-(1) (Isopropenyl chloride).
CH₃CCLCH₃; mw 76.53; liq; mp -137.4°; bp 22.65°; d 0.917g/cc at 20/4°; RI 1.3973.
Sol in acet, benz, eth and chl. Prepn is by reacting 1,2-dichloroprene with aq KOH. Expl limits in air are 4.5 to 16%; flash pt is -20°.
Refs: 1) Beil 1, 198, (82), [169], (698) & (737) 2) Bretherick (1975), 355 3) ChemRubHdb (1975), C457

3-Chloropropene-(1) (Allyl chloride).
CICH₂CH₂CH₂; mw 76.53; color liq; mp -134.5°, -136.4° (sep values); bp 45°, 44.6° (sep values); d 0.937g/cc at 20/4°; RI 1.4157.
Sol in acet, benz, eth and chlor. Prepn is by reacting HCl (d 1.19g/cc) with allylalcohol at RT, or by distally allyllic with HCl (20% conc) in a mol ratio of 1:5. Expl limits in air are 3.3 to 11.2%; flash pt is -32°. Allylic chloride is v toxic. The TLV is 1 ppm or 3mgs/cm of air (Ref 1a)
Refs: 1) Beil 1, 198, (82), [169], (768) & (738) 1a Sax (1968), 385 2) Bretherick (1975), 355 3) ChemRubHdb (1975), C457

1,1,1-Trichloro-3-Nitropropene-(2).
CCI₃CH:CHNO₂, mw 190.41; N 7.36%; OB to CO₂ -42.01%; pale yel oil, powerful irritant and lachrmyator; mp -4.4°; bp 44-45° at 1mm, 97° or 99.5° (sep values) at 28mm, d 1.556g/cc; RI 1.5172. Sol in acet, ethanol, eth and aqu soln of NaOH. Prepn is by slowly heating a mixt of 45g of P₂O₃ with 150ml of med heavy USI mineral oil plus 36g of 1,1,1-trichloro-2-hydroxy-3-nitropropene to 170°. The mixt is then cooled and the excess P₂O₃ decomp with ice and w. The nitroolefin product separates as a heavy, yel oil on steam distn. After eth extraction of the aqu distillate the product is redistd at reduced press giving a 46% yield.

The nitroolefin decomp at 150°. The dry (Na or K) salt of this compd is a primary expl

Propen-2-en-1-ol (Allyl alcohol).
CH₃:CH:CH₂.OH; mw 58.09; OB to CO₂ -220.35%; colorli, mobile liq with a pungent odor; mp -129°; bp 96.9°, d 0.8520g/cc at 20/4°; RI 1.4127, 1.4133, 1.4135 (sep values). V sol in w, ethanol and ether. Prepn is by the high temp chlorination of propene, followed by hydrolysis of allyl chloride. Thus, "... Allyl chloride is hydrolyzed at 200psi pressure, 150°C and a pH range of 10-12. Injection of steam forms a water-allyl alcohol azeotrope, which is then treated with diallyl ether to remove water. Final purifcation by distillation leads to a 98% min assay ..." (Ref 2). Using procedures such as the above, "... at least two American companies (Shell Chemical Co and Dow Chemical Co) produce a total of several million lbs per year..." (Ref 2)

Allyl alcohol is an expl with expl limits in air of 2.5 and 18%; an open cup flash pt of 32°, a Qc of 7617cal/g and an autoign when point of 443°.

The alcohol has an LD₅₀ of 0.064kg/kg in rats; an acute toxicity, LD₅₀, of 0.053ml/kg, found by penetration of rabbit skin. The liq is rapidly absorbed by the skin and distributed thru the body. The vap is highly irritating to the respiratory tract and to the eyes (Refs 2 & 3). The TLV is 2ppm or 5mgs/cc of air (Ref 2a)

Prop-2-en-1-thiol (Allyl mercaptan).
CH₃:CH:CH₂.SH; mw 74.15; bp 63-6°; d

P 475
0.9304g/cc at 20/4°C; RI 1.4680. Prep'n is by reacting allyl bromide with K hydrogen sulfide in aq ethanol. Allyl mercaptan has a flash pt of −10°C.

Refs: 1) Beil 1, 440, (226), [478], (1888) & (2095) 2) Bretherick (1975), 367

Propargols and Derivatives. See under “Liquid Propellants” in Vol 7, L34-R to L44-R


β-Propiolactone (Propanoic acid, 3-hydroxy lactone).
CH₂=CH₂
O — C=O; mw 72.07; OB to CO₂ − 133.20%;
liq; mp −33.4°C; bp 155°C, 162°C (rapid decomp) (sep values); d 1.1460g/cc at 20/4°C; RI 1.4105. Sol in eth, w and chl. Prep'n is by adding formaldehyde to ketene in the presence of Zn chloride. The lactone has a lower expl level in air of 2.9% and a flash pt of 75°C.

β-propiolactone is the most toxic of the lactones. It is a strong irritant and has produced skin cancer in exp'tl animals. The TLV is none


Propionic Acid (2-Propanoic acid, Propionic acid or Acetylenecarboxylic acid). CH₃C₂O₂H; mw 70.05; OB to CO₂ − 114.20%; liq; mp 9°C (cryst from CS₂), 18°C (anhyd); bp 144°C (decomp); d 1.1380g/cc at 20/4°C; RI 1.4302, 1.4306 at 20/4°C (sep values). V sol in acet, eth, ethanol, chl and w. Prep'n is by reacting acetylene magnesium bromide with carbon dioxide in ether


2-Nitro-Phenylpropionic Acid (2-Nitrophenyl propionic acid).

\[
\text{C}_6\text{H}_5\text{C}=\text{C}\text{CH}_2\text{CO}_2\text{H}
\]

mw 191.15; N 73.38%; OB to CO₂ − 138.11%; colorl ndles or Is; mp 157°C (decomp); bp, expls. Sol in eth and ethanol; sl sol in chl. Prep'n is by nitration of phenylpropionic acid or by treating α,β-dibromo-β-[2-nitrophenyl]-propionic acid with an excess of NaOH and then hydrolyzing with HCl to ppt the product
Ref: Beil 9, 637, (267), [438] & (3067)

Propionaldehyde and Derivatives

Propionaldehyde (Propanal, Propylaldehyde, Propyl aldehyde, Propional or methylacetaldehyde). CH₃CH₂CH₂:O; mw 58.09; OB to CO₂ − 220.35%; colorl liq with suffocating odor; mp −81°C; bp 48.8°C; d 0.8058g/cc at 20/4°C; RI 1.3636. V sol in ethanol and eth; sol in w. Prep'n is by treating propyl alc with Na bichromate oxidizing mixt contg sulfuric acid and then distg off the aldehyde. Also, by passing propyl alc vap over Cu at high temp. Propanal has expl limits in air of 2.9 to 17%, a flash pt of −9°C to −7°C, and an autoign temp of 207°C.

The aldehyde has a min oral lethal concn in rats of 800mgs/kg and a min inhalation concn for rats of 8000ppm/4 hrs


α,β,β-Trinitro-Propionaldehyde, Dipotassium Salt of [Dipotassium-2,3,3-Trinitropropanol-1)]. CK(NO₃)₂,CK(NO₃)₂CHO; mw 269.25; N 15.61%; OB to CO₂ 2.97%; red-yel ndles; mp, v sens, deton violently. V sol in w. Prep'n is by reacting 20g of K nitrate with 20g of mucobromic acid in 70cc of ethanol at 30−35°C. The salt deflagrates on contact with either concd
sulfuric or hydrochloric acid


**Propionates and Derivatives**

[2-Nitro-Ethyl]-Propionate.

\( \text{C}_9\text{H}_5\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2; \text{mw} 147.15; \text{N} 9.52\%; \text{OB to CO}_2 -114.15\%; \text{colorl mobile liq; mp, when distd above 150° the compd deton; bp } 106.0 \text{ to 108.2° at 10mm; d } 1.1727 \text{g/cc; RI } 1.4336. \text{ Prepn is by reacting at a boil 2-nitro-ethylalcohol with propionic acid in benz solvent, with concd sulfuric acid as the coupling reagent. The prod is recovered by vac distn Ref: Bell 2, (524)}

[1-Nitromethyl-2-Methyl-Propyl]-Propionate.

\( \text{C}_9\text{H}_{16}\cdot\text{CO}_2\cdot\text{CH}(_2)\cdot\text{NO}_2\cdot\text{CH}(_2)\cdot\text{NO}_2; \text{mw} 189.24; \text{N} 7.40\%; \text{OB to CO}_2 -164.85\%; \text{liq; bp ca 238–45° (decompon); d } 1.0655 \text{g/cc; RI } 1.43563. \text{ Prepn is by reacting propionic acid anhydride with 4-nitropentanol at 60° using concd sulfuric acid as the coupling reagent. The prod is recovered by vac distn Ref: Bell 2, (529)}

[2-Nitro-Propyl]-Propionate.

\( \text{C}_9\text{H}_{16}\cdot\text{CO}_2\cdot\text{CH}(_2)\cdot\text{NO}_2\cdot\text{CH}(_2); \text{mw} 161.18; \text{N} 8.69\%; \text{OB to CO}_2 -134.00\%; \text{colorl liq; mp, when heated over 150° the compd deton; bp } 106.8 \text{ to 107.0° at 10mm; d } 1.1201 \text{g/cc; RI } 1.42815. \text{ Prepn is by reacting at a boil 2-nitro-propyl alcohol with propionic acid using benz as the solvent, and concd sulfuric acid as the coupling reagent. The prod is recovered by vac distn Ref: Bell 2, (525)}

**Propionic Acid and Derivatives**

**Propionic Acid (Methylacetic acid, Propionic acid or Ethyl formic acid).** \( \text{CH}_3\text{CH}(_2)\cdot\text{CO(OH)}; \text{mw} 74.09; \text{colorl oily liq with rancid odor; mp, -20.8°, -21.5° (sep values); bp } 140.7°, 140.99°, 141.1° (sep values); d } 0.9930 \text{g/cc; RI } 1.3869, 1.3862 \text{ (sep values). Sol in ethanol, eth, chlf and w. Obt’d from natural gas by the Fischer-Tropsch process; as a by-product in the pyrolysis of wood; by the action of microorganisms on a...
variety of materials in small yields. The acid has a flash pt of 54°, an ign temp of 513°, and a Qc of -367 kcal/mole.

Propionic acid is an irritant to skin, eyes and mucous membranes. The oral LD₅₀ for rats is 4290 mg/kg.


α-Azido Propionic Acid Azide.
CH₃.CH(N₃)_2.CO.N₂; mw 140.13; N 59.99%; OB to CO₂ 79.93%; pungent yel oil. Sol in eth. Prepn by reacting a soln of acetone-[α-azido-propionyl-hydrazone] in one normal HCl with a concd aq soln of Na nitrite in the presence of some eth. The azide expd on heating.

Ref: 1) Beil 2, (115) 2) T. Curtius & H. Franzen, Ber 45, 1037-44 (1912) & CA 6, 2433 (1912)

β-Azido Propionic Acid Azide.
N₃.CH₂.CH₂.CO.N₂; mw 140.13; N 59.99%; OB to CO₂ 79.93%; pungent yel oil. Sol in eth. Prepn by reacting a soln of acetone-[α-azido-propionyl-hydrazone] in one normal HCl with a concd aq soln of Na nitrite in the presence of some eth. The azide expd on heating.

Ref: Beil 2, (115)

β-Azido Propionic Acid (L-2-Azido propionic acid or dl-α-Triazo propionic acid).
CH₃.CH(N₃)₂.CO₂H; mw 115.11; N 36.51%; OB to CO₂ 90.35%; oily liq; mp 0°, bp 97.5° at 3mm, d 1.2502 g/cc at 33°. Sol in eth; sl sol in w. Prepn is by heating an ethanolic soln of the ethyl ester with an aq soln of 1 g equiv wt of KOH. The azide expds on heating.

The Ag salt, Silver β-Azido Propionic Acid, AgC₃H₄O₂N₃; white ndles; sl w sol, also expds on heating.


α-Nitro Propionic Acid. CH₃.CH(NO₂)₂.CO₂H; mw 119.09; N 11.76%; OB to CO₂ 60.46%; ndles, mp 61-61.5° (decompn). V sol in w, ethanol, eth, benz, chf3; sl sol in ligroin and carbon disulfide. Prepn is by boiling the ammonium salt of α-nitro ethyl propionate with alc NaOH. The Na salt is then hydrolyzed with HCl.

Ref: Beil 2, (114)

β,β-Dinitro-Propionic Acid[3,3-Dinitro-Propionic acid-(1)]. (O₂N)₂CH.CH₂.CO₂H; mw 164.09; N 17.08%; OB to CO₂ 19.55%; viscous grn oil; mp, expds on heating. Prepn is by hydrolysis of β,β-dinitropropionic nitrile with concd HCl.

Ref: Beil 2, 263

3,3,3-Triiodopropionic Acid. Cl₃.CH₂.CO₂H; mw 451.76; OB to CO₂ 19.48%; lt yel prisms; mp 131° (decompn). Sol in eth, ethanol, warm benz (decompn); insol in w. Prepn is by heating iodopropionic acid with HI (d 1.96 g/cc) on a steam bath.

Ref: Beil 2, (575)

Propionic Nitrile. See "Ethyl Cyanide" in Vol 6, E223-L

Propionyls and Derivatives

3-Pentanone (Propionone, Diethyl ketone or DEX). See under this title in this Vol

Bis-[α(?)]-Bromo-Propionyl]-Amine.
(CH₃.CHBr.CO₂NH; mw 286.96; N 4.88%; OB to CO₂ 80.84%; ndles (from hot w); mp 148° (decomp occurs at about 152°). V sol in hot w, ethanol and eth. Prepn is by exposure of the α-bromopropionic acid amide bromide to moist air.

Ref: Beil 2, 256
Propionyl nitrite (Nitric acid-propionic acid anhydride). CH₃CH₂.CO.O.NO; mw 103.09; N 13.59%; OB to CO₂ -85.36%; golden-yellow liq; bp 40°C (decomp). Prepn is by reacting nitrosyl chloride with Ag propionate. The nitrite is a weaker exp than acetyl nitrite. It is quickly depolymerized by light.

Ref: Beyl 2, 243 & (108)

N-Propionyl-Dimethylsulfiminim-Dihydrochloride.
C₂H₅.CO.N:S(CH₃)₂.HCl; mw 163.63; N 8.56%; OB to CO₂ -117.34%; crystals; mp 110°C (decomp). Soln in w and warm org solvents. Prepn is by reacting N-Chloropropionamide dissolved in eth with dimethyl sulfide dissolved in CCl₄ at below 0°C.

Ref: Beyl 2, (551)

2-Propyl Acetate, 1,1,1-Trinitro.
H₃C.C(O).O.CH.C(NO₂)₃;

CH₃
mw 237.15; N 17.72%; OB to CO₂ -37.11%; colorless liq; bp 56°C at 1 mm; RI 1.4432. Prepn is by reacting nitroform with vinyl acetate. The compd burns quietly with a blue flame and detonates weakly from a heavy hammer blow.


Propyl Acrylate (Propionic Acid, Propyl ester). The (theoretical) parent compd for nitroolefin polymers used as propyls and expls such as "2,2-Dinitropropionylacrylate (DNPA)." See under this title in this Vol, N139-R to N140-L.

CH₂:CH.C(NO₂)₃C₃H₇; mw 114.16; colorless liq; bp 122.9°C; d 0.91996g/cc at 0°C. Prepn is by reduction with Zn in sulfuric acid of the propyl ester of α,β-dibromopropionic acid dissolved in n-propanol.

Ref: Beyl 2, 400 & (1225)

1,1,1-Trinitro-2-Propyl Acrylate.
H
CH₃.C.O.C(O).CH:CH₂
C(NO₂)₃

N-Propionyl-N,2,4,6-Trimethyl-2,4,6-trinitro-aniline (N-Nitro-N-propyl-2,4,6-trinitro-aniline, Propyl Tetryl or Propyl-picycl-nitramine).
(O₂N)₃C₆H₄·N(NO₂).CH₂.C₂H₅; mw 315.5; N 22.2%; OB to CO₂ -73.6; colorless leaflets; mp 98°, 97° (separate values), sol in ethanol. Prepn is by reacting picyclnitrile with K propylnitramine in warm ethanol. The compd is an expl.

Ref: Beyl 12, 771 & (371)

2,4,6-Trinitro-N-(iso-propyl)-Aniline.
(O₂N)₃C₆H₄·NH.CH(CH₃)₂; mw 270.2; N 20.74%; OB to CO₂ -100.64%; yellow needles; mp 106-7°C. Sol in acetone and hot ethanol. Prepn is by nitrating 2,4-Dinitro-N-(iso-propyl)-aniline with hot anhydrous nitric acid. The compd is an expl.

Refs: 1) Beyl 12, 764 2) A. Mulder, Rec 25, 116 (1906) & CA, not found

Propyl Aniline and Derivatives

Propyl Aniline (Phenylpropylamine).
C₆H₅·NH·(CH₃)₂·CH₂; mw 135.21; bp 222°C, d 0.9443g/cc at 20/4°C; RI 1.5428. Sol in ethanol, eth and lig. Prepn is by reacting aniline with propyl alcohol over silica gel at 385°C.

Ref: Beyl 12, 166, (159), [94] & (264)

N-Propionyl-N,2,4,6-Tetracyano-2,4,6-trinitro-aniline (N-Nitro-N-propyl-2,4,6-trinitro-aniline, Propyl Tetrayl or Propyl-picycl-nitramine).
(O₂N)₃C₆H₄·N(NO₂).CH₂:C₂H₅; mw 315.23; N 22.2%; OB to CO₂ -73.6; colorless leaflets; mp 98°, 97° (separate values), sol in ethanol. Prepn is by reacting picyclnitrile with K propylnitramine in warm ethanol. The compd is an expl.

Ref: Beyl 12, 771 & (371)
2,4,6-Trinitro-N-(iso-propyl)-N-Nitraniline (Iso-
propylpikrylnitramin in Ger).
\((O_2N)_3C_6H_2(NO_2)CH(CHOH)_3\); mw 315.23; N
22.22%; OB to CO\(_2\) - 73.60%; pale yel crys-
s; mp 107–8\(^\circ\); d 1.563g/cc at 10\(^\circ\). Sol in ethanol.
Prepn is by nitration of 2,4-dinitroisopropyl-
aniline with hot anhyd nitric acid. The compd
is an expl
Refs: 1) Beil 12, 771 2) A. Mulder, Rec
25, 115 (1906) & CA, not found

Trinitro Propyl Bromide.
\((O_2N)_2C_2H_2CH_2Br\); mw 258.0; N 16.29%
; OB to CO\(_2\) - 12.40%; yel liq. Prepn is by re-
acting powd Ag \(\gamma\)-trinitrobutyrate and bromine
in carbon tetrachloride. The bromide burns
rapidly and can be deton with a hammer blow
Refs: 1) Beil, not found 2) Anon. "Syn-
thesis of New Explosives & Propellants", Quar-
terly Progress Rept No 7, US Rubber Co, Passaic,
Contract Nord 10129 (1949), 10 & 11

2,2-Dinitropropyl Trinitrobutyrate (DNPTB).
\((O_2N)_2C_2(CH_2)_2OC(O)_2CH_2C(NO_2)_2CH_3\;
; mw 355.21; N 19.72%; OB to CO\(_2\) - 29.28%
; waxy crys; mp 93\(^\circ\); d 1.66g/cc. Prepn is by
reacting 2,2-dinitropropanol with butyric acid
chloride in chf in the presence of anhyd Al
chloride. DNPTB has a hot bar ign temp of
300\(^\circ\) and an impact sensy of about that of
TNT (151cm for the 50% pt using a 2.5kg wt
with No 12 tools in an ERL machine). Vac stab
is 0.5ml of gas (100\(^\circ\) for 48 hrs)
Refs: 1) Beil, not found 2) W.F. Sager &
D.V. Sickman, "Second Report on Research and
Development in New Chemical High Explosi-
es", NAVORD 483 (1952), 24 3) D.
Jensen, "The Preparation of 2,2,2-Trinitroethyl-
4,4-dinitropentanoate", NAVORD 2498 (1952)
4) M. Hill, "Preparation and Properties of 2,2-
Dinitropropanol Esters", NAVORD 2497 (1952)

Propyl-[-2,4,6-Trinitro-phenyl]-Ether (Picricacid-
propyl ether or Propylpicrate).
\((O_2N)_2C_2H_2OCH_2CH_2CH_3\); mw 271.21; N
36.87%; OB to CO\(_2\) - 91.44%; colori ndles; mp
43\(^\circ\). V sol in all org solvents. Prepn is by
adding a warm soln of picryl chloride dissolved
in n-propyl alc to an ice-cold soln of KOH in
n-propyl alc. The orange ppt formed is then
hydrolyzed with dil aq HCl to form a yel solid.
The crude ether is then dissolved in benz and
treated with decolorizing carbon. Final pptn is
then performed using lig. The yield is 61\%.
The lead block test of the ether has shown it
to be 68% as powerful as TNT
Refs: 1) Beil 6, 290 2) H. Blatt & A.W.
Bytina, JACS 72, 3274–75 (1950) & CA 44,
10673 (1950)

2,2-Dinitropropyl Fumarate (DNPF).
\(CH_3C(NO_2)_2CH_2O.CO.CH.CH.CO.O.CH_2C(NO_2)_2CH_3\;
; mw 380.24; N 14.74%; OB to CO\(_2\) - 58.91%
; waxy crys; mp 84\(^\circ\); d 1.60g/cc. Prepn is by re-
acting 2,2-dinitropropanol with fumactic acid
chloride in chf soln in the presence of anhyd.
Al chloride. DNPF has a hot bar ign temp of
269\(^\circ\) and an impact sensy that approaches TNT
Refs: 1) Beil, not found 2) W.F. Sager &
D.V. Sickman, "Second Report on Research and
Development in New Chemical High Explosi-
es", NAVORD 483 (1952), 27

Propylmalonolazidic Acid.
\(CH_3C(CH_2)_2C(CO_2C_2H_5)(CO.N_3)\); mw 198.23;
N 21.20%; OB to CO\(_2\) - 153.36%; yel oil, expl.
Sol in eth and CCl\(_4\). Prepn is by reacting the K
salt of the half (or mono) ethyl ester of propyl
malonic acid with nitrous acid
Refs: 1) Beil, not found 2) T. Curtius & W.
Lehmann, "Transformation of alkylated malonic
acids into \(\alpha\)-amino acids. III. Synthesis of \(\alpha\)-
aminaoaleric acid, propylmalonolazidic acid . . .",
JPraktChem 125, 211–302 (1930) & CA 24,
3215 (1930)

Propyl Malonic Acid Diazeide.
\(C_2H_5.CH_2.CH(CO.N_3)_2\); mw 196.20%; N
41.84%; OB to CO\(_2\) - 114.17%; yel, v odiferous
oil; mp, v unstable. Prepn is by reacting propyl-
malonic acid-dihydradize with Na nitrite in cold
dil HCl
Ref: Beil 2, (1730)
Bis(2,2-Dinitropropyl) Nitramine (DNPN).

\[ \text{CH}_2\text{C(ONO}_2\text{)}_2\cdot\text{CH}_2\text{N(NO}_2\text{)}_2\cdot\text{CH}_2\text{C(ONO}_2\text{)}_2\cdot\text{CH}_3 \]

mw 254.21; N 33.07%; OB to CO\textsubscript{2} −44.06%;
crysts; mp 187−88° (decomp); d 1.726g/cc.
Sol in hot methanol and methyl ethyl ketone.
Prepn is by nitration of bis(2,2-dinitropropyl) amine at 30−35° using mixed acid (HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4}/free SO\textsubscript{3} in the following percentages: 35.2/53.4/11.6). The yield is 94%.

DNPN has a booster senso using gaps consisting of Al plates and a LA donor of 0.053′′ (Tetryl = 0.0736′′); a gap test using Al gaps and Tetryl as the acceptor of 0.177′′ (Tetryl = 0.160′′); an ignition temp of 236°; an impact senso of 28.5cm using a 2.5kg wt and a vac stab of:

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>cc of gas in 48 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.22</td>
</tr>
<tr>
<td>120</td>
<td>0.32 (Tetryl=1.42)</td>
</tr>
<tr>
<td>140</td>
<td>0.16 (Tetryl=58.0)</td>
</tr>
</tbody>
</table>

in 8 hrs)


Nitropropylsonitramine, Sodium salt.

\[ \text{C}_2\text{H}_4\text{C(ONO}_2\text{)}_2\cdot\text{NaNO}_2\cdot\frac{1}{2}\text{H}_2\text{O} \]

mw 202.10; N 20.80%; OB to CO\textsubscript{2} −43.54%;
small ndles, deliq; mp, expls with great brisance when heated. V sol in w. Prepn is by reacting nitropropylsonitramine with an alcoholic soln of NaOH.

Ref: Bell 1, 631.

n-Propyl Nitrate (NPN). C\textsubscript{2}H\textsubscript{5}CH\textsubscript{2}O.NO\textsubscript{2};
mw 105.125; N 13.33%; OB to CO\textsubscript{2} −98.93%;
white liq; fl p 102°; bp 110.5°; d 1.0538
g/cc at 20/4°; R1 1.3973 (Ref 1), 1.3983 (Ref 4).
Sol in ethanol and eth. Gelanitizes NC.
Forms azeotropic mixts with butyl alc, acetic acid, heptane, toluene, nitroethane, perchloroethylene, w, etc. Prepn is by reacting propyl alc with concd nitric acid (d 1.41g/cc) dissolved in ethylacetate at 20°, followed by distn of the product. NPN can also be prepd by reacting a continuous stream of propyl alc below the surface of stirred mixed acid (20% nitric acid, 68% sulfuric acid and 12% w by wt) in a cooled (0−5°) open stainless steel vessel. Addnl mixed acid is also simultaneously introduced at about a third of the depth of the liq. An overflow pipe maintains a constant reactant level and the effluent prod is sep, washed with 10% eq Na carbonate soln and dried by passage thru a Filtrol packed tower. Contact time of reactants can vary from 0.6 to 15 mins using about 50% isopropanol at 0° to yield 66.5% NPN (Ref 3b).

Lik NPN can be deton with difficulty at RT in a Trauzl block using a No 8 blasting cap with w tamping; a mixt with kieselguhr, however, readily detonates with an expansion of 230cc vs 200cc for AN (Refs 1a & 6). By raising the temp of the liq NPN to over 90°, the BuMines was able to propagate deton in a steel pipe of 1-3/8″ ID and 1/8″ wall thickness using a Tetryl charge. The avg deton vel is 5100m/sec (Ref 4).

Much work has been done on the adiabatic compression ignition of NPN vapor mixed with various gases by both NOL (Ref 2) and Brit Imp Chem Inds (Ref 4). A table of compression ratios and resultant temps from the deton of NPN vapor saturated gas mixts is presented below.

NPN is completely compatible with the following materials: hard copper, ST aluminum alloy, 28 soft aluminum, K Monel, 303 stainless steel and polyethylene. The compatibility limit for 10-20 cold-rolled steel is one year (Ref 4).

However, according to Harvey (Ref 3a), addn of as little as 0.05% of a polyhydric alc such as glycerol to NPN will prevent the corrosion of steel.

The work of the BuMines (Ref 5) in measuring the effect of NPN/air compn on deton vel is presented in Table 1:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Air</th>
<th>Nitrogen</th>
<th>Carbon Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explosive Ratios</td>
<td>13.5:1 to 21.5:1</td>
<td>33.5:1 to 40:1</td>
<td>No expls at 80:1</td>
</tr>
<tr>
<td>Calculated Temps</td>
<td>322° to 695°</td>
<td>890° to 985°</td>
<td>795°</td>
</tr>
</tbody>
</table>
Table 1
NPN Vapors Content vs Detonation Velocity

<table>
<thead>
<tr>
<th>NPN Vapor, volume percent</th>
<th>Detonation Velocity, m/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>no ignition</td>
</tr>
<tr>
<td>2.4</td>
<td>no ignition</td>
</tr>
<tr>
<td>2.5 (estimated)</td>
<td>215 (deflagration)</td>
</tr>
<tr>
<td>2.7</td>
<td>1,455</td>
</tr>
<tr>
<td>2.8</td>
<td>1,480</td>
</tr>
<tr>
<td>3.5</td>
<td>1,630</td>
</tr>
<tr>
<td>4.1</td>
<td>1,520</td>
</tr>
<tr>
<td>5.0</td>
<td>1,620</td>
</tr>
<tr>
<td>6.7</td>
<td>1,740</td>
</tr>
<tr>
<td>21.2</td>
<td>1,900</td>
</tr>
<tr>
<td>31.4</td>
<td>1,525</td>
</tr>
</tbody>
</table>

The expln temp under confinement with a heating rate of 5°F/min is 190°F. The self-ignition temp of a vas/air mixt is 193°F. The principle prod of the thermal decompn of NPN is carbon monoxide. The combined molr vol from one mole of NPN of carbon monoxide and carbon dioxide is 1.84 moles (at 305 psi and 200°F). NPN has a flash pt (Abel closed cup) of 65°F and (Cleveland open cup) of 78°F.

A card gap value of 16 cards has been obtained for NPN using the ERDE procedure (Ref 4) at temps ranging from −14° to +15°. Under the same conditions, a value of 24 cards was found for Nitromethane.

The vol of gas evolved from the thermal decompn of 1 kg of NPN is 1000X at 250 psi and 1050°C.

NPN has a Q of 40800 cal/g (liq H₂O at 25° ref); a Q of 4000 cal/g (liq H₂O at 25° ref); and a Q of 660 cal/g (Ref 4). It has a bond energy level of 0 of 37 kcal/mole (Ref 8).

NPN is v sl hygroscopic; it is, however, miscible with w in a ratio of 1/3 and 13/7 (w/NPN), forming azetropes which boil at 84.8° and 107.5°, respectively (Ref 1).

Impact sensy has been deterd for NPN using a modified Imp Chem Ind app (Ref 4) which consists of a sample cylinder 1/2” in diam and 1” long, fitted with a piston upon which a wt of 310g is dropped. Results were dtr for both air and nitrogen by varying the vol of the gas above the liq NPN. These data are tabulated below.

Impact sensy has also been reported on by Médard (Ref 2b). Using a 15mg sample wt, he dropped a 5kg wt a height of 293cm, obtaining a weak expln in 48 out of 100 drops. The 50% prob pt is 10m, while NG has a 50% prob pt of 0.40m.

Again, from the work of Ref 4, power by BallMort is 0.1 (Mk 1 mortar using a No 6 ASA AI CB detonator; PA=100) and 72.9 (Mk IIIC mortar using a No 8 ASA AI CB detonator; PA=100). Power by Trauzl test is 13cc/g (40% of NG).

No explns were obtd in 15 shots each of 0.303 ball or AP ammo against targets consisting of 3 cu inch mild steel boxes with walls of 1/16", 1/8" and 3/16" thickness contg NPN. Ref is 55% explns using eth nitrate as the filler for this rifle bullet impact test.

Table 2 correlates data from refs 4 and 5 on the sensy to initiation of NPN.

The specific heats of NPN product gases (primarily carbon monoxide and carbon dioxide) arising from combustion are C_p 0.346 cal/g/° and C_v 0.252 cal/g/° at 300°F. The specific impulse of these gases (calc at 400 psi) is 155 lbs/thrust/lb/sec.

The result of high temp stability testing shows that at a temp of 150–200°F under a press greater than 100 psi, NPN will undergo a self-sustained thermal decompn yielding a gaseous mixt comprised primarily of carbon monoxide.

A conclusion drawn from the data of both Refs 4 and 5 is that NPN is completely stable at ambient temp and does not deteriorate on prolonged storage. Recommended storage procedures include packaging NPN in polyethylene or lead-lined 55 gal drums constructed of stainless steel, aluminum or aluminum alloys; a temp range that should not exceed 160°F; blanketing under nitrogen; a storage period of no longer than one year; and treatment as a high expl and storage in accordance with the American

<table>
<thead>
<tr>
<th>Gas in Vapor Space</th>
<th>Air</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol of gas, cc</td>
<td>1.35</td>
<td>0.86</td>
</tr>
<tr>
<td>Drop height, cm</td>
<td>10 to 15</td>
<td>5 to 10</td>
</tr>
<tr>
<td>Calc'd expln temp, °</td>
<td>&lt;400</td>
<td>&lt;400</td>
</tr>
</tbody>
</table>
**Table 2**

<table>
<thead>
<tr>
<th>Type of Initiation</th>
<th>Catalytic Cr &amp; Ni Metal Rings</th>
<th>Spark</th>
<th>Hot Wire</th>
<th>Inert Shock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Energy Input</td>
<td>Thermal (elec heaters)</td>
<td>Thermal (ionized gas)</td>
<td>Thermal (elec)</td>
<td>Mech Comprsn</td>
</tr>
<tr>
<td>Min Energy Reqd</td>
<td>—</td>
<td>—</td>
<td>~5kJoules</td>
<td>755psig/＜1 sec</td>
</tr>
<tr>
<td>NPN State</td>
<td>Liq spray in air</td>
<td>Vapor</td>
<td>Vapor</td>
<td>Vapor</td>
</tr>
<tr>
<td>% NPN in mixt</td>
<td>3 in air</td>
<td>3 in air</td>
<td>4.5 in air</td>
<td></td>
</tr>
<tr>
<td>Min Temp, °C</td>
<td>200°</td>
<td>34°</td>
<td>34°</td>
<td>30.8°</td>
</tr>
<tr>
<td>Min Press, cm Hg</td>
<td>Ambient</td>
<td>120</td>
<td>120</td>
<td>74</td>
</tr>
<tr>
<td>Time to initation, sec</td>
<td>~1</td>
<td>0.01</td>
<td>&gt;2</td>
<td>&lt;1 \textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ref 8 indicates that a Mach 3 shock initiation of NPN droplets in oxygen can occur in 24.1 microsecs

**Table of Distances (Ref 5)**

According to Sax (Ref 7) NPN is highly toxic, having a min tolerance level of 25ppm or 110mgs per cubic meter of air.

NPN is used as a rocket monopropellant, a jet motor starting fuel; its hot combustion prod gases are used to drive turbine type motors (Ref 4). It is also used as a degreasing solvent for iron and aluminum (Ref 2a), and as a diesel fuel additive (Ref 3a). Proposed uses for NPN are in expls or ammo monopropellants (Addnl Refs, limited distribution Nos 1, 2, 4 and 5 to 8).

The viscosity of NPN at 20° is 0.66 centipoise

The vapor press of NPN can be cale by any one of the three equations shown below. The results of such cals over a range of temps are given in Table 3 (Ref 4)

\[
\log_{10} P = 33.42 - 3090/T - 8.7 \log_{10} T, \quad \text{where } P \text{ is in mm Hg and } T \text{ is in } ^\circ\text{K};
\]

\[
\log_{10} P = 7.3506 - 1520/(t+230), \quad \text{where } P \text{ is in mm Hg and } t \text{ is in } ^\circ\text{C};
\]

\[
\log_{10} P = 7.246 - 1444/(t+221), \quad \text{where } P \text{ is in mm Hg and } t \text{ is in } ^\circ\text{C}.
\]

The heat of vnp of NPN is 73.4 to 81.8cal/g (Ref 4)

Refs: 1) Beil 1, 355, [369] & [1419]
1a) Naoum, NG (1928), 208 2) ADL Pure-ExplCompsds I (1947), 31 & 141 2a) W. Klabunde, “Solvent for Degreasing Iron and Aluminum”, USP 2435312 (1948) & CA 42,


**Table 3**

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Vapor Press (mm Hg) according to Eqn No</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>30</td>
<td>43</td>
</tr>
<tr>
<td>40</td>
<td>69</td>
</tr>
<tr>
<td>50</td>
<td>106</td>
</tr>
<tr>
<td>60</td>
<td>157</td>
</tr>
<tr>
<td>70</td>
<td>226</td>
</tr>
<tr>
<td>80</td>
<td>317</td>
</tr>
</tbody>
</table>


2-Nitro Isopropyl Nitrate.

\[ \text{CH}_3\text{C(NO}_2\text{)}\text{CH}_3; \text{mw} 150.11; \text{N} 53.29\%; \text{O}_\text{NO}_2 \text{ OB to CO}_2 -42.64\%; \text{color oil; bp} 71^\circ \text{ at} 1 \text{ mm; d} 1.348\text{gc/cc at} 20/4^\circ, \text{RI} 1.447; \text{sol in eth; insol in w. The nitrate is polymerized to the 1-nitropropene polymer (qv) by aq NaOH. Prepn is by reacting propene with N}_2\text{O}_4 \text{ in eth at} 0^\circ \text{ for} 3 \text{ hrs. The oily prod is w washed and dried by distn with benz. It is sepd by vac distn from other nitration prods in a 21.4% yield. The nitrate has 75% of the power (lead block) of blasting gelatin and is v insens to friction and impact.} \]

Refs: 1) Beil 1, (1477) & (1497) 2) N. Levy & C.W. Scaife, JCS 1946, 1093–96 & CA 41, 2388 (1947)

Isopropyl Nitrate (IPN). \[ \text{CH}_3\text{(H)C(NO}_2\text{)}\text{CH}_3; \text{mw} 105.125; \text{N} 13.33\%; \text{OB to CO}_2 -98.93\%; \text{w white liq with an ethereal odor; fp -82^\circ; bp 101.5^\circ; d 1.049\text{gc/cc at} 15.5/15.5^\circ; \text{RI} 1.3913. \text{Sol in ethanol and eth. There are four methods of prepn which are used for IPN prod: a) that of Silva (Ref 2) in which isopropyl iodide and powd Ag nitrate are reacted to give a 69% yield; b) that described by Naoum in Ref 4 in which acet is catalytically reduced and nitrated; c) also mentioned by Naoum is a procedure involving usage of the gases from oil cracking stills; and d) a continuous process patented by Allen & Tobin (Ref 4a) and developed almost simultaneously by Desseigne (Ref 5), in which isopropyl alc is nitrated continuously by dropping a mixt of 61% nitric acid with 95% isopropylalc, satd with urea, into a vessel contg boiling 50% nitric acid. The IPN and w formed are continuously distd off at about 98^\circ from the reaction mixt. The vol of the reaction mixt is held constant by drainage of nitric acid and unstable by-products from it as the reactants are added. A curtain of air, nitrogen or carbon dioxide is blown thru the reaction mixt to improve mixing and to facilitate the elimination of the volatile prods. However, a flow of inert gas in excess of 50l/hr decreases the IPN yield. The optimum ratio of nitric acid to isopropyl alc is about 2:1. The IPN yield is 78%.

According to Brochet (Ref 8), IPN can be detod in thick-walled tubes of plastic with an ID of 16mm at 20^\circ using a Gevelot P 53A electric igniter coupled to a Briska #8 detonator, used in conjunction with an HE donor (75% PETN). The donor, in turn, is in direct contact with the liq IPN. Under these conditions a deton vel of 5400m/sec is achieved. Ref 6 lists a liq IPN deton vel of 5070m/sec in 1½" mild steel pipes. Also, the conditions under which deton is propagated are stated by Ref 6 to be as follows; viz,

"... (a) At 70^\circ C and above when confined in a mild steel pipe 30 inches in length of 1.5 inch ID and 0.2-inch wall thickness and initiated with 3 oz Tetryl. (b) Along the full length of a similar pipe 5 ft in length in which the detonation was initiated in a region at 70^\circ C (top 2 feet) and propagated thru a region at 15^\circ C (bottom 3 ft) (c) At 35^\circ C when confined in a mild steel
canister 10 inches in diameter and 0.5-inch wall thickness and initiated with 8 oz Tetryl.

(d) At 10°C in a container 2 inches in diameter and 1.5-inch wall thickness and initiated with 4 oz Submarine blasting gelatine and 1 oz Tetryl.

(e) Between 30°C and 45°C and above in stainless steel pipes 30 inches in length and 1.55 inches in diameter and 0.66-inch wall thickness and initiated with 3 oz Tetryl . . ."

Again, according to Ref 6, deton is propagated in a 1½" diam mild steel tube at ambient temp using a No 8 detonator alone when IPN is mixed with kieselguhr or sawdust in the ratio of 1 p solid/2 p IPN by wt. Mixts. with sand (4 p/1 p IPN by wt) are detonatable under the same conditions using 1.5 oz PETN.

The work of Ref 6 includes parameters affecting the adiabatic compression ignition of NPN vapor mixed with various gases. A table of compression ratios and resultant temps from the deton of the IPN vapor satd gas mixts is presented below.

The compatibility of IPN with a great number of matls has also been investigated by the authors of Ref 6. These data are presented in tabular fashion below.

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>Nitrogen</th>
<th>Carbon Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Explosive Ratios</strong></td>
<td>13.5:1 to 21.5:1</td>
<td>33.5:1 to 40:1</td>
<td>No explns at 80:1</td>
</tr>
<tr>
<td><strong>Calculated Temps</strong></td>
<td>525°C to 695°C</td>
<td>890°C to 985°C</td>
<td>795°C</td>
</tr>
</tbody>
</table>

To serve as a basis for comparison a series of IPN solns were prep’d as test matl reactants:

1. Pure IPN
2. IPN + oleic acid (0.3%)
3. IPN + methanol (4%) + oleic acid (0.3%)
4. IPN + isopropanol (4%) + oleic acid (0.3%)
5. IPN + Esso Aviation Turbo-Oil 35 (EEL3) (2%)
6. IPN + methanol (4%)
7. IPN + isopropanol (4%)
8. IPN + isopropanol (4%) + EEL3 (2%)
9. IPN + Shellex 4 (1%)
10. IPN + isopropanol (4%) + Shellex 4 (1%)
11. IPN + cyclohexanol (5%)

Table 1 details the effects of exposure of a variety of metals and alloys to the solns enumerated above.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Solution No</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel 18/8/Ti</td>
<td>1–11</td>
<td>No Corrn</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>1, 5</td>
<td>V sl corrn; 2x10^-3 mm/yr</td>
</tr>
<tr>
<td></td>
<td>2, 3, 4, 6, 7</td>
<td>Some corrn; pptn of rust</td>
</tr>
<tr>
<td></td>
<td>8, 9, 10</td>
<td>No corrn; a little staining</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Corrn; no pptn</td>
</tr>
<tr>
<td>Tinplate</td>
<td>1, 2, 3, 4, 8, 9, 10</td>
<td>No corrn; sl staining</td>
</tr>
<tr>
<td></td>
<td>5, 6, 7, 11</td>
<td>Bad staining</td>
</tr>
<tr>
<td>“Kynal” P.10 Aluminum</td>
<td>1, 2, 3, 4, 6, 7, 8</td>
<td>No corrn</td>
</tr>
<tr>
<td></td>
<td>9, 10, 11</td>
<td>No corrn</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>V sl corrn</td>
</tr>
<tr>
<td>“Kynal” M35/1 Aluminum Alloy</td>
<td>1, 2, 3, 4, 6, 7, 8</td>
<td>No corrn</td>
</tr>
<tr>
<td></td>
<td>9, 10, 11</td>
<td>No corrn</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>V sl corrn</td>
</tr>
<tr>
<td>“Kynal” M39/2 Aluminum Alloy</td>
<td>1, 2, 3, 4</td>
<td>No corrn</td>
</tr>
<tr>
<td>“Kynal” PA.19 Aluminum Alloy</td>
<td>1, 2, 3, 4</td>
<td>No corrn</td>
</tr>
<tr>
<td>Electrolytic Zinc</td>
<td>1, 4</td>
<td>No corrn</td>
</tr>
<tr>
<td></td>
<td>2, 3</td>
<td>Hvy white ppt of Zn oleate</td>
</tr>
<tr>
<td>Lead</td>
<td>1</td>
<td>No corrn; Pb content of liq &lt;1 ppm</td>
</tr>
<tr>
<td></td>
<td>2, 4</td>
<td>Hvy ppt of Pb oleate</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Corrn 5.7x10^4 mm/yr; Pb content 7 ppm</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Corrn 6.2x10^4 mm/yr; Pb content 54 ppm</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>No corrn</td>
</tr>
<tr>
<td></td>
<td>3, 4</td>
<td>Ppt of Cd oleate</td>
</tr>
<tr>
<td>Copper</td>
<td>1</td>
<td>No corrn; sl staining</td>
</tr>
<tr>
<td>70-30 Brass</td>
<td>1</td>
<td>No corrn; sl staining</td>
</tr>
<tr>
<td>Chromium</td>
<td>1</td>
<td>No corrn</td>
</tr>
<tr>
<td>Nickel</td>
<td>1</td>
<td>No corrn</td>
</tr>
</tbody>
</table>
II. Rubbers and Synthetic Materials

Table 2
Compatibility of IPN with Rubbers and Synthetic Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Results</th>
<th>Recommendation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone rubbers S80, S90, B30</td>
<td>Vol increases (approx 60%) and sample loses elasticity</td>
<td>Unsuitable</td>
</tr>
<tr>
<td>Hycar rubber</td>
<td>Vol increases and sample rots</td>
<td>Unsuitable</td>
</tr>
<tr>
<td>Chloroprene Acrylonitrile rubber</td>
<td>Vol increases and sample loses elasticity</td>
<td>Unsuitable</td>
</tr>
<tr>
<td>Butyl rubber B100</td>
<td>Vol increases and sample softens</td>
<td>Unsuitable</td>
</tr>
<tr>
<td>Synthetic rubber JP73</td>
<td>No deterioration</td>
<td>Suitable</td>
</tr>
<tr>
<td>Nylon</td>
<td>Sample becomes brittle</td>
<td>Unsuitable</td>
</tr>
<tr>
<td>Perspex</td>
<td>Sample dissolves</td>
<td>Unsuitable</td>
</tr>
<tr>
<td>Polythene</td>
<td>Sample not attacked</td>
<td>Suitable</td>
</tr>
<tr>
<td>Fluron (P.T.F.E.)</td>
<td>Sample not attacked</td>
<td>Suitable</td>
</tr>
<tr>
<td>P.V.C.</td>
<td>Sample becomes brittle</td>
<td>Unsuitable</td>
</tr>
</tbody>
</table>

III. Various Common Liquids

Table 3
Compatibility of IPN with Common Liquids

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>The liqs are only slightly miscible</td>
</tr>
<tr>
<td>Battery acid (dil sulfuric acid, sp gr 1.3g/cc)</td>
<td>The liqs were heated together for several days. Initially a brn ring formed at the interface, but this disappeared and no further reaction took place</td>
</tr>
<tr>
<td>44D Lubricating oil</td>
<td>The liqs are miscible at least up to 15% oil and no interaction occurs. A mixt contg 12% oil could be ignited in a turbo-starter but the reaction was not self-sustaining</td>
</tr>
<tr>
<td>RDE/0/463 Lubricating oil</td>
<td>The liqs are miscible at least up to 17% oil and no interaction occurs. A turbo-starter operated on a mixt contg 17% oil</td>
</tr>
<tr>
<td>Kerosene</td>
<td>This was mixed with pure IPN and IPN contg the above oils. No reaction occured and a turbo-starter operated satisfactorily</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Glycol is only v sl sol in IPN. No interaction occurs</td>
</tr>
</tbody>
</table>
The flash pt for IPN using the Abel closed cup method is 53°F while the Cleveland open cup method gives a value of 72°F. Min spont ign temp range in air on a heated brass, Al, stainless steel or mild steel plate is 245–60°F.

The following data from Ref 6 present, in tabular form, the limits of flammability of IPN vapor/air mixts over a press and temp range:

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Lower Limit Vol, %</th>
<th>Upper Limit Vol, %</th>
<th>Pressure, psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>18–19</td>
<td>2.4</td>
<td>To Satn Pt</td>
<td>14.7</td>
</tr>
<tr>
<td>89</td>
<td>2.2</td>
<td>5%</td>
<td>14.7</td>
</tr>
<tr>
<td>125</td>
<td>1.8</td>
<td>–</td>
<td>5</td>
</tr>
<tr>
<td>125</td>
<td>1.2</td>
<td>–</td>
<td>70</td>
</tr>
<tr>
<td>125</td>
<td>1.0</td>
<td>–</td>
<td>250</td>
</tr>
<tr>
<td>125</td>
<td>0.95</td>
<td>–</td>
<td>500</td>
</tr>
<tr>
<td>125</td>
<td>0.90</td>
<td>–</td>
<td>1000</td>
</tr>
</tbody>
</table>

The ign temps obtd by passing IPN vapor/air mixts thru a heated glass tube are tabulated below (Ref 6):

<table>
<thead>
<tr>
<th>Composition (Vol % IPN)</th>
<th>Ignition Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>No ignition up to 500°</td>
</tr>
<tr>
<td>3.8</td>
<td>240</td>
</tr>
<tr>
<td>4.6</td>
<td>220</td>
</tr>
<tr>
<td>12.6</td>
<td>200</td>
</tr>
<tr>
<td>28.2</td>
<td>190</td>
</tr>
<tr>
<td>46.2</td>
<td>200</td>
</tr>
</tbody>
</table>

IPN gave a ERDE gap test (Scale III) of 16 cards at ambient temp. A value of over 27 cards is indicative of positive sens to the rifle bullet test. Refs as to gap sensy include ethylene oxide (10 cards), Nitromethane (24 cards) and ethyl nitrate (43 cards)

The vol of gas evolved on the thermal decompn of 1 kg of IPN is 10000 at 250 psi and 1050° (Ref 6). The temp obtd by cordite detonation of IPN is 1027–1277° (Ref 10)

IPN has a Q<sub>i</sub> of 4110 cal/g (liq H<sub>2</sub>O at 25° as ref), a Q<sub>c</sub> of 44000 cal/g (liq H<sub>2</sub>O at 25° as ref), a Q<sub>v</sub> of 630 cal/g (w vap as ref at 100°), a Q<sub>T</sub> of 660 cal/g and a Q<sub>vap</sub> of 70.5 or 79.5 cal/g (Ref 6)

Tavernier and Lamoureux (Ref 5a) present a somewhat different set of thermal data; viz., a Q<sub>c</sub> of 445.6 kcal/g or 468.3 kcal/mol; a Q<sub>i</sub> of 4455.1 kcal/g or 468.2 kcal/mol; a P<sub>T</sub> of 489.3 kcal/g or 54.4 kcal/mol; and a P<sub>v</sub> of 549.7 kcal/g or 54.6 kcal/mol

IPN has a hygroscopicity at 20° of 0.095% and at −20° of 0.03%

Impact sensy has been found for IPN by a modified Imp Chem Ind app (Ref 6) which consists of a sample cylinder ½ inch in diam and 1 inch long, fitted with a piston upon which a wt of 310 g is dropped. Results were found for both air and nitrogen by varying the vol of the gas above the liq IPN. These data are tabulated below:

<table>
<thead>
<tr>
<th>Gas in Vapor Space</th>
<th>Air</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol of gas, cc</td>
<td>1.35</td>
<td>0.86</td>
</tr>
<tr>
<td>Drop Height, cm</td>
<td>15 to 20</td>
<td>5 to 10</td>
</tr>
<tr>
<td>Calculated expln temp, °C</td>
<td>&lt;400</td>
<td>&lt;400</td>
</tr>
</tbody>
</table>

Impact sensy has also been detd by Médard (Ref 4b) using a 17 mg sample wt. He dropped a 5 kg wt 293 cm to obtain v weak expls in 46 out of 100 drops. The 50% prob pt for IPN using this procedure was found to be 10w while NG was found to have a 50% prob pt of 0.4m

Again, from the work of Ref 6, power for IPN by BalMort using a Mk I mortar in conjunction with a No 6 ASA Al CB detonator was found to be 0.4; using a Mk IIC mortar with a No 8 ASA Al CB detonator the power was found to be 73.9 (Ref of PA=100). Trauzl test values for IPN are tabulated below:

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Vol, cc/g a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>20</td>
<td>16.5</td>
</tr>
<tr>
<td>30</td>
<td>19</td>
</tr>
</tbody>
</table>

a ethyl nitrate values over this temp are 41–42 cc/g

Table 6 presents the data from Ref 6 on the initiation sensy of IPN.
### Table 6

<table>
<thead>
<tr>
<th>Type of Initiation</th>
<th>Catalytic (Ni &amp; Cr oxides in coke granules)</th>
<th>Spark</th>
<th>Hot Wire</th>
<th>Expl Shock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Energy Input</td>
<td>Thermal (burning of air-fuel mixt)</td>
<td>Thermal (ionized gas)</td>
<td>Thermal (electrical)</td>
<td>Thermal (comprsn)</td>
</tr>
<tr>
<td>Min Energy Required</td>
<td>liq spray in air</td>
<td>4.0 millijoules</td>
<td>5.34 Kjoules</td>
<td>~10 Kjoules</td>
</tr>
<tr>
<td>IPN State</td>
<td>vapor/air mixt</td>
<td>liq</td>
<td>liq</td>
<td>liq</td>
</tr>
<tr>
<td>% IPN in Mixt by Vol</td>
<td>100</td>
<td>5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Min Temp, °C</td>
<td>200</td>
<td>ambient</td>
<td>926</td>
<td>&gt; 250</td>
</tr>
<tr>
<td>Min Press, cm Hg</td>
<td>ambient</td>
<td>ambient</td>
<td>&gt; 1250 psig</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Time to Initiation, sec</td>
<td>~1</td>
<td>0.5</td>
<td>2.170</td>
<td></td>
</tr>
</tbody>
</table>

The specific heats of IPN product gas (primarily carbon monoxide and methane) arising from combustion are $C_p = 0.333$ cal/g°C and $C_v = 0.246$ cal/g°C (both calc'd at 250 psi and 300°C). The specific impulse of these gases (calc'd at 400 psi) is 155 lbs/thrust/sec.

The following data is the result of a series of high temp storage (stability) expts conducted by (Brit) Imp Chem Inds Ltd (Ref 6) on IPN:

a) A summary for a series of pressure development tests involving a steel vessel of 100cc capacity, half filled with IPN, and maintained at a given temp for four hours is presented below:

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Heating Period, Hrs</th>
<th>Pressure Developed, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>135</td>
<td>4</td>
<td>23</td>
</tr>
<tr>
<td>142</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>150</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>160</td>
<td>2</td>
<td>Explds</td>
</tr>
</tbody>
</table>

b) In another series of tests on IPN involving a 500cc steel vessel, the rate of temp rise was recorded at the temps shown. The elapsed time required before decompn occurred at each temp is also shown. The conclusion reached in Ref 6 is that IPN is stable for prolonged periods at storage temps below 100°; at 120° IPN is reasonably stable for periods up to 3 hrs; above that temp, however, decompn occurs.

c) In an attempt to stabilize IPN at 140°, a series of additives were evaluated, unsuccessfully, using a 500cc steel vessel. From the data presented in Table 7 it was concluded that no additive would stabilize IPN since decompn occurred in the vap phase rather than the liq phase.

### Table 7

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Time, Hours</th>
<th>Reaction After &quot;Time&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3</td>
<td>Decompn</td>
</tr>
<tr>
<td>130</td>
<td>2</td>
<td>Decompn</td>
</tr>
<tr>
<td>150</td>
<td>&lt; 0.5</td>
<td>Decompn</td>
</tr>
</tbody>
</table>

**Evaluation of Additives for IPN Stabilization**

<table>
<thead>
<tr>
<th>Additive (%)</th>
<th>Mean Rate of Pressure Increase, (psi/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl iodide (2%)</td>
<td>0.6</td>
</tr>
<tr>
<td>Lead tetraethyl (0.1%)</td>
<td>0.7</td>
</tr>
<tr>
<td>Oxamide (satd)</td>
<td>1.0</td>
</tr>
<tr>
<td>Urea (satd)</td>
<td>1.0</td>
</tr>
<tr>
<td>Methyl centralte (1%)</td>
<td>1.1</td>
</tr>
<tr>
<td>2-Nitrodiphenylamine (1%)</td>
<td>1.1</td>
</tr>
<tr>
<td>None</td>
<td>1.2</td>
</tr>
<tr>
<td>Acetone (2%)</td>
<td>1.7</td>
</tr>
<tr>
<td>Carbon tetrachloride (2%)</td>
<td>1.8</td>
</tr>
<tr>
<td>Acetamide (satd)</td>
<td>2.4</td>
</tr>
<tr>
<td>Trichloroethylene (2%)</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Table 8

<table>
<thead>
<tr>
<th>Test No</th>
<th>Relief Valve Setting, psig</th>
<th>Heating Time Reqd for Valve Operation, min</th>
<th>Temp Increase Range Of IPN, °C</th>
<th>Volume IPN Lost, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>60</td>
<td>130–143</td>
<td>55.05</td>
</tr>
<tr>
<td>2</td>
<td>40–45</td>
<td>28</td>
<td>145–150</td>
<td>26.77</td>
</tr>
<tr>
<td>3</td>
<td>No Relief Valve – Disc Burst at 110psig</td>
<td>33½</td>
<td>145</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>No Relief Valve – Disc Burst at 200psig</td>
<td>52</td>
<td>&gt; 159</td>
<td>100</td>
</tr>
</tbody>
</table>

d) In a final series of tests on IPN high temp storage conditioning, a 2-gal aluminum container filled with IPN and filled with a bursting disc relief valve, thermocouples and a press gauge, was heated by total immersion in an oil bath maintained at 150°. The results of these tests are shown in Table 8.

IPN storage recommendations are the same as for NPN (see the previous entry).

The toxicity of IPN is evaluated by Ref 6 as follows:

(a) When inhaled as a vapor or adsorbed thru the skin, IPN acts as a vasodilator and produces a headache in the same manner as other organic nitrates;
(b) When injected subcutaneously into rats at the rate of 4cc/kg body wt, it was concluded that the max allowable concn is 100ppm; and
(c) When rats were exposed to different concn levels of IPN in air the following resulted:

(1) At 4% by vol deep anesthesia occurred in 30 mins and death in 2 hrs (3 rats); (2) At 2% by vol deep anesthesia was reached in 4 hrs, but the rats recovered within 24 hrs, after a total exposure of 6 hrs; and (3) At 0.2% by vol no ill effects were observed from 10 exposures of 6 hrs each.

IPN is used as a rocket monopropellant, a jet motor starting fuel, and its hot combustion prod gases are used to drive turbine type motors (Refs 6, 8 and 9). Other uses are in exps and proplnts (Addnl limited distribution Refs 1 to 4).

The viscosity of IPN at 20° is 0.66 centipoise.

The vap press of IPN can be calcd by either one of two equations shown below. The results of such calcns over a temp range are given in Table 9.

(1) \[ \log_{10}P = 29.08 - 2780/T - 7.3 \log_{10}T, \]
where P is in mm Hg and T is in °K; and
(2) \[ \log_{10}P = 7.303 - 1457/(t+227.5), \]
where P is in mm Hg and t is in °C.

Table 9

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Vapor Pressure (mm Hg) according to Eqn No</th>
<th>Vapor Pressure Measured, mm Hg (Ref 4c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>404</td>
<td></td>
</tr>
</tbody>
</table>


**n-Propyl Nitrite (Nitrous acid n-propyl ester).**
$(\text{CH}_3\text{CH}_2\text{O})_{\text{NO}}$; mw 89.09; N 15.72%; 
OB to CO$_2$ $-134.70$; liq; bp 47.75$^\circ$; d 0.8864 
$g/cc$ at 20$/4^\circ$, 0.935g/cc at 21$^\circ$; RI 1.3592, 1.3613 (separate values). Sol in ethanol and eth.
It forms azeotropic mixts with acet, carbon disulfide, pentane, propyl chloride, etc. Prepn is by reacting a mixt of n-propanol and Na nitrite with dils sulfuric acid. Compl prepn (Ref 2) consists of spraying an excess of nitric acid on vaporized propane at 400 to 1300$^\circ$F and from 115 to 175 psi in an adiabatic reactor.

Vap inhalation causes vasodilatation, smooth muscle relaxation and hypotension.

N-propyl nitrate is used as a jet proplnt


**Iso-Propyl Nitrite (2-Propanol nitrite or Nitrous acid isopropyl ester).**
$(\text{CH}_3\text{CH}_2\text{O})_{\text{NO}}$; mw 89.09; N 15.72%; OB to CO$_2$ $-134.70$; pale yel oil; bp 40.0$^\circ$; d 0.844 at 25/4$^\circ$; RI 1.3520.
It forms azeotropic mixts with methylol, carbon disulfide, isopentane, isopropyl halides, isoprene, etc. Prepn is by treating isopropyl alc with nitryo chloride. Also, by passing NO$_2$ into isopropyl alc in 25–30$^\circ$. Compl prepn is similar to that of n-propyl nitrite (above). The nitrite has a flash p of <10$^\circ$.

According to Merck (Ref 5), "... isopropyl nitrite can cause vasodilatation with fall in blood pressure, tachycardia, headache. Large doses can cause methemoglobinuria with cyanosis. Severe poisoning results in shock which can end fatally ..."

Iso-Propyl nitrite is used as a jet proplnt, a jet proplnt additive and as an additive to diesel fuels

Propyl Nitric Acid. See in this Vol, N135-R

N,N'-Bis(Trinitropropyl) Oxamide.
\((\text{O}_2\text{N})_2\text{C.C.CH}_2\text{CH}_2\text{NH.CO.CONH.(CH}_2\text{)}_2\text{C(NO}_2\text{)}_3;\) mw 442.26; N 25.34%; OB to \text{CO}_2 -25.32%;
crysts; mp 195–97° (decompn); d 1.692g/cc.
Prepn is by reacting 3,3-trinitropropylamine with oxalyl chloride. The oxamide has a hot
bar ign temp of 215° and an impact sensy about that of Tetryl
Refs: 1) Bell, not found 2) L.T. Carleton & M.B. Frankel, "Explosives Research", Rept No
711, Aerojet-Genl Corp, Azusa, ONR contract N7onr-462 (1953) 3) W.F. Sager & D.V
 Sickman, "... Research and Development in New Chemical High Explosives", NAVORD
486 (1954)

N,N'-Dinitro-N,N'-Bis(Trinitropropyl) Oxamide.
\((\text{O}_2\text{N})_3\text{C(CH}_2\text{)}_2\text{N(NO}_2\text{)}_2\text{.CO.CO.N(NO}_2\text{)(CH}_2\text{)}_2\text{C(NO}_2\text{)}_3;\) mw 532.26; N 26.32%; OB to \text{CO}_2 -6.01%;
crysts; mp, exists in two isomers with different mp's, 125–26° and 128–29°. Prepn is by ni-
tration of N,N'-bis(trinitropropyl) oxamide. The oxamide has a hot bar ign temp of 202° and an
impact sensy approaching that of PETN
Refs: 1) Bell, not found 2) L.T. Carleton & M.B. Frankel, "Explosives Research", Rept No
711, Aerojet-Genl Corp, Azusa, ONR contract N7onr-462 (1953) 3) W.F. Sager & D.V
 Sickman, "... Research and Development in New Chemical High Explosives", NAVORD
486 (1954)

Propylpenterythritol Trinitrate Ether.
See in this Vol under “Pentaerythritol Propyl Ether Trinitrate”

Iso-Propyl Peroxides. See under “Peroxides” in this Vol

2,2-Dinitropropyl Phosphate.
\(\text{CH}_3\text{C(NO}_2\text{)}_2\text{.CH}_2\text{O}_2\text{PO; mw 463.30; N 18.14%; OB to \text{CO}_2 -56.98%; crysts; mp 155°.}\)
Prepn is by reacting 2,2-dinitropropanol with pentachloride. The phosphate has an impact

Bis (2,2-Dinitropropyl) Succinate. See Vol 5, D1500-L (information incomplete).
\(\text{CH}_3\text{C(NO}_2\text{)}_2\text{.CH}_2\text{O}_2\text{.C.C(CH}_2\text{)}_2\text{CO.CH}_2\text{C(NO}_2\text{)}_2\text{.CH}_3;\) mw 382.28; N 14.66%; OB to
\text{CO}_2 -62.78%; crysts; mp 84–85°; d 1.51g/cc.
Prepn is by reacting dinitropropanol with succinyl chloride. The ester has a hot bar ign temp of
> 400°
Refs: 1) Bell, not found 2) W.F. Sager & D.V. Sickman, "... Research and Development in New Chemical High Explosives", NAVORD
486 (1954)

Bis(Trinitropropyl) Sulfone. See under “3,3,3',3',3' - Hexanitropropyl-sulfone...” in Vol 5, D1501-L

Bis(Trinitropropyl) Urea. See under “Dipropylureas and Derivatives” in Vol 5, D1501-L & R

[N'-Isopropyl-Ureido] - Acetic Acid Azide (5-Isopropyl-hydantoin acid azide).
\((\text{CH}_3\text{)}_2\text{CH.NH.CO.NH.CH}_2\text{CO.N}_3\text{H; mw 185.22; N 37.82%; OB to \text{CO}_2 -133.89%; mp ca 100°}\)
(delifrates quickly when heated). Prepn is by reacting [N-isopropyl-ureido] - acetic acid-hydra-
زيد with Na nitrite dissolved in aq HCl
Ref: Bell 4, (1169)
Propylene and Derivatives. See Propylene under "Polypropylene" in this Vol. The Derivatives are listed under "Propene and Derivatives", also in this Vol

Propylene Dinitramine (PDNA). See under "Diaminopropane and Derivatives" in Vol 5, D1143-R

Propyleneglycols and Derivatives. See under "1,2- and 1,3-Propane Diol and Derivatives" in this Vol. For "Propyleneglycol", see under "Glycols and Derivatives" in Vol 6, G112-L to G114-R. Addnl propylene glycol compds of interest are presented next

3-Azido-1,2-Propylene glycol Dinitrate (3-Azido-1,2-propanedinitrate or Dinitroazidohydride), (O₂N₂)₂CH₂CH(ONO₂)₂CH₂N₃; mw 207.13; N 33.82%; OB to CO₂ -19.3%; liq; mp, explds on heating. Prepn is by reacting glycerin monochlorohydridin with Na azide, and then nitrating the resulting prod. The azide has a calcd power of 162% PA and is extremely sensitive

Refs: 1) Beil, not found 2) Blatt, OSRD 1085 (1942), 3) ADL Punch Cards 1 (1947), 48 4) Ibid 71 (1954) (Conf)

Di(2,2-Dinitro-1,3-Propylene glycol)-Trinitro Butyrate. (O₂N₂)₂C₂H₄(O.C)(O).CH₂C(NO₂)₂H.OC(ONO₂)₂CH₂; mw 576.31; crys; mp 144°; d 1.68g/cc. Prepn is by the addn of nitro to the acrylate ester of 2,2-dinitro-1,3-propylene glycol or by the addn of acryl chloride to the glycol. The compd has an ign temp of 235° and an impact sensy about that of Comp A. It was hoped that the ester could be used as a casting medium, but its high mp and low d were unsatisfactory for ml purposes


Nitropropylene. See under "Propene and Derivatives" as 1-, 2-Nitro and Di-Nitro Propenes in this Vol

Propylene Oxide (1,2-Epoxypropane, Methyl-oxirane or Prepene Oxide).

CH₂CH.CH₃; mw 58.08; OB to CO₂ -220.39%; colorless liq, ether-like odor; mp -104.4°; bp 35°; d 0.859g/cc at 0/4°; RI 1.3670. V sol in ethanol, eth and w. Prepn is by treating propylene chlorohydrin with an aq soln of KOH. The oxide has expl limits in air of 3.1 to 27.5%, 2 to 22% (separate values); an autoign temp of 465°; a flash pt (open cup) of -37°; a Q₂ of 7771.3cal/g. The compd deto weakly and burns with a clear blue flame. It may flash-back a great distance from an ign source. It also polymerizes in contact with highly active catalysts such as bases, releasing v large amts of heat resulting in an expln when confined

Propylene oxide has an LD₅₀ (oral-rat) of 1140mgs/kg and a respiration lower tolerance level vol of 100ppm (Refs 7, 8 & 9)

It is used as an intermediate in the synthesis of various chemicals; as a low-boiling solvent for gums, resins, NC, etc; it is also considered a candidate for use in fuel-air munitions

Propyleneoxazone, C\textsubscript{3}H\textsubscript{6}O\textsubscript{4} (structure ?); mw 106.11; OB to CO\textsubscript{2} -75.39%; a sticky oil of unknown odor; bp 28-34\textdegree; d 1.0672 g/cc at 22\textdegree; RI 1.37978 at 22\textdegree. Prepn is by reaction of propene and ozone dissolved in ethyl chloride and cooled using a mix of carbon dioxide and ether. The ozonide is a strong expl.
Ref: Beil. 1, (82)

Bis-Propylene Pseudonitrosite.

CH\textsubscript{3}CH\textsubscript{2}NO\textsubscript{2}

N.O.O.N

CH\textsubscript{3}CH\textsubscript{2}NO\textsubscript{2} (Ref 2); mw 236.22; N 23.72% (calc), 26-26.9% (found); OB to CO\textsubscript{2} -81.28%. Prepn is by reacting N\textsubscript{2}O\textsubscript{3} with propylene in eth at a temp of 5 to 20\textdegree. Marshall (Ref 2) proposed the compd for use as a base charge.
Ref: 1) Beil. 1, 198 & (260, 695), listed as the propylene pseudo nitrosite (C\textsubscript{3}H\textsubscript{6}N\textsubscript{2}O\textsubscript{3})
2) J. Marshall, USP 1473825 (1923) & CA 18, 588 (1924)

Iso-Propylidene-Dicyclohexylidene-Triperoxide.
See in Vol 2, B144-R

Iso-Propylidene-2,4,6-Trinitro-Phenylhydrazine

(Acetone-[2,4,6-trinitro-phenyl hydrazone] or Acetone-pyridylhydrazone).

(O\textsubscript{2}N\textsubscript{3})\textsubscript{2}C\textsubscript{3}H\textsubscript{6}NH:N:C(CH\textsubscript{3})\textsubscript{3}; mw 283.23; N 24.73%; OB to CO\textsubscript{2} -93.21%; yel ndles; mp 125\textdegree, decmps at 130\textdegree. V sol in benz, clhf, acetic acid and eth acetate; sol in ethanol and eth. Prepn is by boiling a mix of pyridylhydrazone and acet in ethanol.
Ref: Beil 15, 495

Propyne. See under “Methyl Acetylene” in this Vol, M94-R

Prosperit V. An older Brit permitted expl contg AN 60, Na nitrate 5, meal 4, nitrotoluenes 6, alkali chloride 21, and NG 4%. OB to CO\textsubscript{2} +2.7%; Pb block expansion 235cc
Ref: Naoum, NG (1928), 434

Proteins, Nitrated. Proteinaceous or albuminoid materials (glue, bones, hides, leather, hair, feathers, etc) can be nitrated in a two-stage process to yield expl yol oils. Thus, glue is treated first with 3.6 pts by wt of 66\textdegree B\textsuperscript{E} sulfuric acid and 2.7 pts of 36\textdegree B\textsuperscript{E} nitric acid. The resultant oil is sep from the heavier spent acid and nitrated further with 3 pts of oleum and 2.6 pts of 36\textdegree B\textsuperscript{E} nitric acid. Both nitrations are conducted at 15-20\textdegree, and never above 40\textdegree. The resulting oily expl can be used alone or mixed with other materials.

To prepare a gelatinous expl, mix with stirring 4 pts of collodion cotton dissolved in 10 pts of acet, 6 pts of “nitrated glue”, and 1 pt of castor oil (to increase the flexibility of the product). After evap the acet, the mass can be cartridge.

To prepare a granular expl, the above procedure is used, except that the castor oil is replaced by an equal wt of mononitronaphthalene. About 80% of the acet is evap, and the mass extruded in any desired shape. Or, the acet can be almost completely removed, and the mass rolled into sheets which can be cut to any desired size.
Ref: 1) V. Gallarati, BritP 358116 (1930) & CA 26, 6141 (1932) 2) M. Bonotto, USP 2411145 (1946) & CA 41, 865 (1947)

Protol or Protoglycerin. See Fermentol in Vol 6, F14-R

Proving Ground (PG). An area or location where equipment, ammo, or weapons are tested or proved.
Ref: Anon, OrdTechTerm (1962), 239-L

Proximity Fuze. See Vol 4, D918-R to D921-R
"PRP" Wax. A waxy substance composed of a mix of petroleum, rosin and paraffin. It was used in Dynamite manuf for coating grains of AN to render them non-hygrosopic.

Sorenson patented an expl suitable for blasting operations which contained AN 100, Mn dioxide 15, petroleum naphtha 6, rosin 15, paraffin 6, potato flour 8, Al 30, and NG 100 pts.

Ref: E. Sorenson, USP 1709498 (1929)

Prussian Fire (Feu Prussian in Fr). See under Wigfall Powder


PTX-1. An expl developed at PicArsn during WWII for use in land mines and demolition charges. It contained Tetryl 50, RDX 30 and TNT 20%; mw 252; OB to CO =-9%, to CO$_2$ =-45%; mp, eutectic 67°, pouring temp 90-95°; d (cast) 1.68g/cc; exudes at 65° and above; sol in acet. Prep by adding the appropriate wt of w-wet RDX to 40/60 Tetrytol previously melted in a steam-jacketed melt kettle. Heating and stirring are continued until all the w is evaporated and the mix is uniform in compn. It can also be prepd by adding Tetryl to Composition B.

Blast. Relative to TNT in air; impulse 109%, peak press 111%.

Brisance. Sand test, 54.8g vs 43.0g for TNT; plate dent test, method B, 127% TNT.

Compatibility with metals. Does not affect Al or mild steel, wet or dry.

Detonation velocity. 7400-7655m/sec for an unconfined cast charge 1 inch in diam, d 1.68 g/cc; vs 6900m/sec for TNT.

Fragmentation test. In 3-inch HE shell, wt of charge 0.864 lbs, d 1.63g/cc: total number of fragments 685 vs 514 for TNT.

Fragment velocity. At 9 ft, 2690ft/sec; at 25.5 ft, 2460ft/sec.

Hygroscopicity. Wt gain after 15 days at 30°, 95% RH: nil.

Impact sensitivity. Bu Mines app, 2kg wt, 44cm vs 100+cm for TNT; PicArsn app, comparable to Tetrytol.

Initiation sensitivity. Can be detonated by 0.23g of MF or 0.22g of LA; does not require a booster.

Rifle bullet sensitivity. About 40% of trials affected by 0.30 cal bullet fired at 90 ft.

Stability. 100° Vac Stab test: 3cc/5g/40 hrs.

Note: A PTX-3 compn, prep by the addn of Halexite to 40/60 Tetrytol, also offered promise in applications where the charge would not be required to withstand 65° storage without exudation.


PTX-2. An expl developed at PicArsn during WWII intended to replace the more sensitive Pentolite. There were two types, with almost identical properties:

<table>
<thead>
<tr>
<th>% by Wt</th>
<th>RDX</th>
<th>PETN</th>
<th>TNT</th>
<th>mw</th>
<th>OB to CO</th>
<th>OB to CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>44</td>
<td>28</td>
<td>28</td>
<td>244</td>
<td>-3%</td>
<td>-33%</td>
</tr>
<tr>
<td>PETN</td>
<td>28</td>
<td>26</td>
<td>33</td>
<td>243</td>
<td>-4%</td>
<td>-36%</td>
</tr>
<tr>
<td>TNT</td>
<td>28</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

mp, eutectic 75°, pouring temp about 95°; d (cast) 1.71g/cc; does not exude at 65°.

Its properties, as examined at PicArsn, were as follows:

Blast. Relative to TNT in air; impulse 113%, peak press 113%.

Brisance. Sand test, 56.9g vs 53.0 for Pentolite and 43.0 for TNT; plate dent test, method B, 141% TNT for cast unconfined PTX-2, d 1.71g/cc.

Compatibility with metals. Does not affect Al, dry or wet; does not affect mild steel, dry.

Detonation velocity. 8000-8065m/sec for an unconfined cast charge 1 inch in diam, d 1.70 g/cc; vs 7500m/sec for Pentolite and 6900m/sec for TNT.

Fragmentation test. In 3-inch HE shell, wt of charge 0.897 lbs, d 1.70g/cc: total number of fragments 750 vs 514 for TNT.

Fragment velocity. At 9 ft, 3020ft/sec; at 25.5 ft, 2850ft/sec.
Friction sensitivity. Crackles with steel shoes
Hygroscopicity. Wet gain after 15 days at 90% RH: nil
Impact sensitivity. BuMines app, 2 kg wt, 35 cm
vs 100+ cm for TNT; PicArsn app, 10 inches vs
9 inches for Pentolite and 14 inches for TNT
Initiation sensitivity. Can be detonated by 0.21 g
of MF, and does not require a booster
Power. BalMort test, 138–45% of TNT, 130%
Pentolite
Rifle bullet sensitivity. About 60% of trials
affected by 0.30 cal bullet fired at 90 ft, vs
92% affected for Pentolite
Shaped charge effectiveness. Steel cone, hole
volume 130% TNT
Stability. 100° Vac Stab test: 2.6 cc/5 g/40 hrs;
120° Vac Stab test: 11 cc/5 g/40 hrs
Uses. Shaped charges and fragmentation weap-
on. Field tests showed that PTX-2 is superior to
Pentolite
PTX-2 can be prep'd by adding the appropriate
wt of w-wet RDX to 30/70 Pentolite previously
melted in a steam-jacketed melt kettle. Heating
and stirring are continued until all the w is
evapd and the mix is uniform in compn. It can
also be prep'd by adding w-wet PETN to Compos-
ite B
Note: A PTX-4 compn, prep'd by the addition
of Halexite to 30/70 Pentolite, also offered prom-
ise, but because of borderline stability in acce-
tered stability tests, it was decided that PTX-4
must be proven by long term storage to be
acceptable for use in standard ammo
Refs: 1) W.R. Tomlinson, "Properties of Ternary
Mixtures of High Explosives," PATR 1414
(1944) 2) A.J. Phillips, "The Manufacture of
PTX-2 by the Slurry Precipitation Process",
PATR 1445 (1944) 3) Anon, "Allied and
Enemy Explosives", Aberdeen Proving Ground
(1946), 131–32  4) Anon, EngrgDesHndbk,
"Explosives Series, Properties of Explosives of
Military Interest", AMCP 706-177 (1971)

Pudrolith (Rockpowder). Blasting expl patented
in 1872 and manuf'd in Engl and Belg. A
typical formulation contained K nitrate 68, S 12,
charcoal 6, sawdust 5, Ba nitrate 3, Na nitrate 3,
and spent tan bark 3%
Ref: Daniel (1902), 653

Pullivitz Explosive. A Ger permissible expl
patented in 1896 contg AN 92.0, phenanthrene
5.5, and K dichromate 2.5%
Refs: 1) Daniel (1902), 659  2) PATR 2510
(1958), Ger 152-L  3) Guia, Dizionario 6
(1959), 375

Pulvrent Ammonium Dynamite. NG 20, AN
25, Na nitrate 36, and dry rye flour 19%
Ref: Daniel (1902), 659

Pulverin. French for meal powder. A special,
finely pulverized BlkPdr consisting of K nitrate
75, S 12.5 and charcoal 12.5%, prep'd by rolling
the ingredients with Pb or lignum vitae balls in
a hardwood barrel. It has been used in pyrotec-
nic applications
Refs: 1) G. Cavaignac, "Livraison de Pulverin
aux Artificiers", MP 3, 29 (1890)  2) Daniel
(1902), 659  3) Davis (1943), 45

Pulvis Fulminans. An older expl, differing in
compn from BlkPdr, contg K nitrate 50.0, S
16.7 and K carbonate 33.3%
Ref: Daniel (1902), 659

Punch Test for Explosives (Stanzprobe in Ger).
See under Brisance Test Methods in Vol 2,
B299-R

Punshon Explosive. Patented in 1870; consisted
of NC soaked for 12 hrs in a sugar soln, and an
oxidizer, such as a nitrate. Another expl, patent-
ed by the same inventor in 1875, was a 70%
Dynamite contg either peat or toasted peas as
absorbants, to which pulverized NC could be
added. The third expl patented by Punshon
(1880) consisted of nitric and picric acids
absorbed on a porous material such as asbesos, and
loaded into cartridges which were painted with
a mixt of Na silicate and powdered glass
Punshon was also the inventor of Oxonite
and Victorte (qv)
Ref: Daniel (1902), 659–60
PVA-4. A semi-plastic expl of Canadian origin, developed during WWII by Dr. Sutherland of Shawinigan Chemicals, Ltd. It contained RDX 90, PVA (polyvinylacetate) 8, and dibutylphthalate 2%. Mw 217; white solid; OB to CO₂ -37%; to CO -10%; softening pt 92°; d (pressed) 1.60g/cc

A practical method of prep this compn was by the addition of a soln of the coating agent to an aq RDX slurry. Based on the quality of the product and the pellet densities obtained, a procedure of adding an acet soln of PVA + DBP to a hot w slurry of RDX, under agitation, was adopted as standard.

In evaluating various types of PVA commercially available in the US, a type obtained from Union Carbide and Carbon, under the trade name “AYAT” was the most promising coating for RDX in the above proportions.

Its properties; as detd at PicArsn, were as follows:

Brisance. Sand test, 58.5g vs 43.0 for TNT
Detonation velocity, 7910m/sec for a cast, unconfined sample 1.0” diam at d 1.60g/cc
Explosion temperature. No cap used; 375° (decomp) after 5 secs; 330° after 1 sec
Friction pendulum test. Unaffected by fiber shoe, cracks on steel shoe
Hygroscopicity. Wt gain at 30° and 90% RH, 0.20%
Impact sensitivity. BuMines app, 2kg wt, 39cm vs 100+cm for TNT; PicArsn app, 9” vs 14” for TNT
Initiation sensitivity. Can be detonated by 0.22g of Pb Azide, and does not require a booster
Loading. Cast or extruded; plasticity 0.3 at 25°, cracked at -40°
Rifle bullet sensitivity. In 5 trials with 0.30 cal bullets fired at 90 ft, 20% explns, 60% burned, 20% unaffected. In 100 trials at -46°, all unaffected
Stability. 100° Heat test: Wt loss 0.10% during first 48 hrs, 0.06% in second 48 hrs; no expln after 100 hrs
Volatility. 0.03% wt loss after 6 hrs at 55° under vacuum
Uses. Demolition charges

Ref 1 states that PVA-4 has sensitivity and stability characteristics considered satisfactory for a demolition expl, and has greater brisance than Composition A or Tetrytol. It undergoes embrittlement when cooled to -40°, but is non-volatile, non-hygroscopic, insol in w, and has such a high softening pt that evaporation in storage is extremely unlikely.


PVN. Acronym for PolyvinylNitrate (see in this Vol)

PW (Poudres de Wetteren). BlkPdrs used by the Fr Navy in larger cal guns. Prior to this, the so-called “Poudres A” were employed

Ref: Daniel (1902), 660

PW. Acronym for White Phosphorus (see in this Vol under Phosphorus, White)

Pyridine and Pyridinium Compounds

Pyridine. C₅H₅N; mw 79.10; flammable, colorless liq, characteristic disagreeable odor, sharp taste; mp -42°; bp 115-16°; d 0.9780 at 25/40°; RI 1.50920 at 20°. Flash pt 20° (closed cup); ignition temp 485°; flammable limits 1.8-12.4%. Vapor may travel considerable distance to a source of ignition and flash back. Vapor forms expl mixts with air (Refs 4 & 5)

There are many methods of prep of pyridine (Ref 2). It is misc with w, alc, eth, petr eth, oils and many other organic liqs.

Pyridine may cause central nervous system depression, irritation of skin and respiratory tract. Large doses may produce gastro-intestinal disturbances, kidney and liver damage (Refs 3 & 4)


**Pyridine Chlorate.** $C_4H_5N.HClO_3$, mw 163.57, N 8.56%, mp 142° (with decomp). Was prep'd by Datta & Choudhury (Ref 3) by evap on a w bath a mixt of a slight excess of pyridine and concd perchloric acid. The resulting crystals of the salt were washed with a small amt of cold w and recrystd from alc. It is sol in w and alc, and insol in non-dissociating organic solvents. When heated, it burns with a sudden flash; it flames when brought into contact with concd sulfuric acid

**Pyridine Perchlorate.** $C_4H_5N.HClO_4$, mw 179.5; N 7.8%; OB to CO$_2$, Cl$_2$ and H$_2$O 80.2%; mp about 288° (without decomp). Can be prep'd by treating pyridine with 20% perchloric acid, and then adding alc to ppt the perchlorate.

Sl sol in w (9.49g in 100ml of soln at 19°); v sl sol in alc (100ml of satd soln in abs alc contains, at 19°, 0.454g; in 95% alc, 1.20g).

Pyridine Perchlorate is almost as powerful as TNT (Pb block expansion 95% TNT, 87% PA), but is much more sensitive to impact (FI 40% PA), being comparable to PETN in this respect (Refs 4 & 5). Kuhn (Ref 7) states that it can be detonated on impact, but is normally considered a stable intermediate, suitable for purification of pyridine. Occasionally explns have occurred when the salt was disturbed (Ref 11), which have been variously attributed to the presence of ethyl perchlorate, AP or chlorates. A safer preparative modification is described (Ref 8). It explds on heating to above 335°, or at a lower temp if AP is present (Ref 10). According to Mellor (Ref 9), the salt can expld violently in contact with metals, while Zacherl (Ref 6) describes a lab expln which occurred during the distn of pyridine liberated from its perchlorate

**Pyridine Picrate.** $C_4H_5N.C_6H_5O_2N_2$, mw 308.22, N 18.2%, gold-yel needles from alc, mp 167–68°. It was prep'd by Ladenburg (Ref 2) by mixing concd solns of pyridine and PA. The salt is difficultly sol in w. It explds when heated rapidly above its mp.


**Pyridine Compounds with Metallic Salts.**

Pyridine combines with many inorganic salts to form additive compds. Some of these are expls, eg:

1) $C_2H_5N.Cu(N_3)_2$: green crysts changing to brown, expls violently ca 202–03° [Beil 20, 191; A. Cirulis & M. Straumanis, ZAnorgChem 251, 350 (1943)]

2) $C_2H_5N.HgCl_3$: orange crysts, expld on heating above 300° (Beil 20, 199)

3) $C_8H_7N.Cr(N_3)_2$: green crysts; expld violently when heated (Beil 20, 62)

4) $C_8H_7N.Cu(ClO_4)_2$: bluish-violet crysts; expld violently when heated (Beil 20, 104–05)

5) $C_8H_7N.Cd(CON)_3$: yellowish crysts; expld weakly when heated (Beil 20, 109)

6) $C_8H_7N.CrO_3.HF$: orange-yel crysts; expld when heated (Beil 20, 113)

7) $C_8H_7N.MnClO_4.3H_2O$: nearly colorl crysts; expld when heated (Beil 20, 115)

8) $C_2H_5N.Zn(ClO_4)_2$: prisms; expld weakly when heated (Beil 20, 108)

**Pyridine Complexes of Metallic Permanganates.**

Pyridine, $C_2H_5N$, like ammonia, forms complexes with various metallic permanganates. In general, they are more or less sol in w and very sol in pyridine. When heated rapidly they expld, but decompose when heated slowly. They burn vigorously when moistened with sulfuric acid or when suddenly compressed. They are unstable and lose pyridine even at RT, and for this reason should be prep'd and dried at 0°.
Cadmium complex. \(4\text{C}_5\text{H}_5\text{N} \cdot \text{Cd(MnO}_4\text{)}_2\); violet tubular crystals, apparently rhombic. It was prepd by mixing concd solns of pyridine (4 moles) and Cd(MnO_4)_2 (1mole) at 0°. V sol in w; explds at about 65°

Cobalt. Could not be prepd

Copper. \(4\text{C}_5\text{H}_5\text{N} \cdot \text{Cu(MnO}_4\text{)}_2\); violet crystals; explds at about 65°. Was prepd by adding a small quantity of pyridine to an aq soln of AgNO_3 and K MnO_4, mixed in equivalent proportions

Nickel. \(4\text{C}_5\text{H}_5\text{N} \cdot \text{Ni(MnO}_4\text{)}_2\); blk pdr; very unstable; decomp at about 65°. Was prepd in the same manner as the cadmium salt

Silver. \(5\text{C}_5\text{H}_5\text{N} \cdot 2\text{AgMnO}_4\); violet needles; explds at about 100°. Was obtained by pouring a mixed soln of AgNO_3 + KMnO_4 into an excess of pyridine, or by gradually adding w to a 50% soln of AgMnO_4 in pyridine

Silver. \(2\text{C}_5\text{H}_5\text{N} \cdot \text{AgMnO}_4\); violet microscopic crystals. Was prepd by adding a small quantity of pyridine to an aq soln of AgNO_3 and K MnO_4, mixed in equal proportions. V sl sol in w; decomp or explds at about 65°

Zinc. \(4\text{C}_5\text{H}_5\text{N} \cdot \text{Zn(MnO}_4\text{)}_2\); violet crystals; v sol in w; explds at about 65°. Was prepd in the same manner as the cadmium salt

Refs: 1) Bell 20, 200 & 203  2) T. Klobb, CR 118, 1271–73 (1894) & JCS 66 (1), 548 (1894)

“Pyro” Abbreviation for Pyrocellulose

Pyrocatechol. See under Di hydroxy benzene and Derivatives in Vol 5, D1270-R ff

Pyrocellulose. See under “Pyrocellulose, Pyro or Pyrocotton” in Vol 2, C105-L ff

Pyrocolok. Trademark for a slow-burning delay train which furnishes a 5-minute delay time in about 10 inches of column length


“Pyrocolloidion” Powder. A smokeless powder developed in Russia about 1891 by Prof. D.I. Mendele’eff, based on NC contg 12.44% N (Pyrocellulose). Its degree of nitration was slightly lower than that of decanitrocellulose, \(\text{C}_2\text{H}_5\text{O}_1\text{O}(\text{ONO}_2)\text{C}_1\text{O}_4\), which has N=12.75%. The reason for using “Pyrocolloidion” was that it contained just enough oxygen for combustion to CO and H_2O. In actual tests, however, some CH_4 and CO_2 were also present in the combustion gases

Trials conducted at Okhta (near St Petersburg) showed that Pyrocolloidion powder was fairly stable, and burned slowly and uniformly. When a 40kg projectile was fired from a 150mm cannon, a muzzle velocity of about 785m/sec was obtained. A Krupp armor plate 36.8cm thick was pierced by a shell weighing 225kg when projected by “Pyrocolloidion” from a 250cm cannon

This powder was so successful that it was adopted not only in Russia (in preference to Vieilles “Poudre B”, developed in Fr), but also by the US Navy. Its introduction in this country was due to Lt. Bernadou, US Naval Attaché in St. Petersburg at that time. Soon after its introduction in the USA (1895–96), the powder was manufd at the Naval Powder Factory, Indian Head, Md. It should be noted that Bernadou improved the powder by using NC with a slightly higher N content (12.6–12.7%), and this became known as “Pyrocellulose Powder”. Its use by the US Army began about 1899

Pyrocolloidion and Pyrocellulose powders belong to the single-base type because they contain only NC and about 1% of a stabilizer, diphenylamine. Both are nearly completely sol in eth-aic mixts. According to microscopic observations conducted by Sapojnikoff (Ref 5), Pyrocolloidion powder is much more uniform than the Fr “Poudre B”, both CP_1 and CP_2 types

Both Pyrocolloidion and Pyrocellulose powders were much “cooler” than powders contg NG (such as Ballistite and Cordite) and caused much less erosion

According to Pérez Ara (Ref 5), the following countries used single-base propLnts until about the beginning of WWII: France, Russia, USA, Argentina, Mexico, Spain, Cuba, Belgium, Switzerland and Rumania, while other countries used either double-base powders exclusively (such as England and Italy), or both single and
double-base powders (Germany and Japan)

Note: Prior to and during WWII, the Germans developed several “cool” propellants in which NG was replaced by Ethyleneglycoldinitrate (EGDN) or Nitrogumidine. They also developed propellants which contained neither NC or NG, such as “Tetrasalz” propellants, which contained Tetramethylanimonitrate


Pyrocore. See Vol 4, D763-L


Pyrocotton or Coton Pyrique. An expl mixt consisting of NC and picrates, proposed in 1883 by Parozzani as a bursting charge for projectiles

Ref: Daniel (1902), 661

Pyrocotton. Same as Pyrocellulose

Pyrodx. Tradename of a close substitute for BlkPdr, invented by D. Pawlak and distributed by the Hodgdon Powder Co, Shawnee Mission, Kansas intended primarily for use with replica sporting firearms. It can be loaded volume-for-volume with BlkPdr, producing similar pressures and velocities. It smokes, smells and fouls somewhat like BlkPdr, and it is claimed that Pyrodx is actually safer to handle and store than modern smokeless powders (Refs 1 & 3)

Pyrodx comes in several types: RS for rifles and shotguns, P for handguns, C for BlkPdr cannon, and CR for BlkPdr centerfire cartridges. It requires very firm bullet-seating, hot percussion caps, and a strong hammer-spring for good ignition – it is not recommended for flintlocks (Ref 3)

Pyrodx is classified as a Class B explosive by the Bureau of Explosives of the Association of American Railroads (Ref 5)

Four persons, including inventor D. Pawlak, were killed in a fire that swept the Pyrodx Corp plant in Issaquah, Washington, on 27 Jan 1977. The plant had been in operation for 13 months. The cause of the fire was not known, and no decision had been made on whether or not to resume operations (Ref 4)


Pyrodialites or Pyrodialytes. A series of expl mixts, patented in Fr by Turpin, beginning in 1881, and contg as principal combustible ingredients, tar (goudron), resin, etc; and as oxidizers, K chloride alone or in mixt with K or Na nitrates. The following examples are taken from Daniel (Ref 2): Extraforte No 0: K chloride 88, tar 10, charcoal 5, Na or Amm bicarbonate 2–3ps; Lente No 2: K chloride 40, NaNitrate 48, tar 20, charcoal 5, Na or Amm bicarbonate 4–5ps. These expls were too “hot”, and were not approved for use in gaseous coal mines

In 1888, Turpin preppl a series of “cool” expls which were permissible, by incorporating materials such as alkali chlorides, Na or K bicarbonate (up to 50% content), fluorides, acetates, oxalates, Ba carbonate,10H2O, chromates, hyposulfites, stannic acid, boric acid, borates, etc, in the expls listed above; eg, a) K chloride 45, double salt of Ca and K acetochlorate 35, tar 18, charcoal 5, and alkali bicarbonate or oxalate 15ps; b) K chloride 15, double salt of K and Amm chlorobichromate 35, or Na nitrate 10, tar 18, charcoal 5, and K or Na bicarbonate 15ps

Due to the fact that chlorates are very sensitive to mechanical action, Turpin replaced them with perchlorates, eg, a) K perchlorate 80, tar 10, and Amm trinitrocreysilate 10%; b) K perchlorate 60, tar 10, & Amm Picrate 30%; c) Amm Perchlorate 85 & tar 15%; d) Amm Perchlorate 75, tar 10, & Amm trinitrobenzoate 15%; and e) Amm Perchlorate 50, tar 10, & Guanidine Nitrate 40%

As an antiacid, 2.5 to 5% Na or Amm bi-
carbonate was added to these compns. By incorporating a cooling agent, such as an oxalate or bicarbonate, permissible expls could be obtained.

Turpin's expls were soon superseded by Cheddites (see Vol 2, C155-L to C164-R), introduced by Street in 1897.

4) Davis (1943), 360

Pyrofulmin or Mercuric Pyrofulminate. See in Vol 6, F223-L.

Pyrofuze. See in Vol 4, D762-R to D763-L

Addnl Refs: 1) Ellern (1968), 207 & 279

Pyrogels. A class of US oil-and-metal incendiary agents. Like napalm (qv), the pyrogels consist essentially of thickened gasoline. The thickener is usually isobutyl methacrylate, and may include natural rubber. Powdered Mg is added to increase the temp of combustion which can reach as high as 1600°, though the pyrogels tend to burn more quickly than napalm. The same type of disseminated incendiary effect is obtained as with napalm-type oil incendiary bombs, but asphalt is added as a binder to overcome the shearing strains resulting from high altitude bombings (Ref 4)

Pyrogels used by the US armed forces include:
1) PT1, which is a complex mixt based on a paste of Mg and an oxidizer, bound with petroleum distillate and asphalt. Isobutyl methacrylate is used as a thickener. 2) PT2, which contains 5% isobutyl methacrylate as a thickener, together with Ba nitrate and a small quantity of asphalt. 3) PT3, which is described as an improved oil and metal incendiary mixt composed of 5% polybutadiene, 6% Na nitrate, 28% Mg, and a trace of p-aminophenol in 60% gasoline (Ref 5)


Pyrogen Igniter. Pyrotechnic igniters contg conventional solid propellant grain rather than pyrotechnic pellets, used mainly in ignition systems for large solid-propellant rocket motors. For solid-propellant rocket motor applications that require spreading the flames from the whole surface of the main charge container of the igniter, a pyrogen igniter with a perforated tube can be used


Pyroglycerin (It). The name given to Nitroglycerin by its discoverer, Ascanio Sobrero, in 1847 (see in Vol 6, G99-R)

Pyroliths. A type of inexpensive "black" powder patented in the 19th century by Matteen. Daniel (Ref 1) states that it contained K or Na nitrate and sawdust, to which could be added Na carbonate or sulfate to the extent of 6%. Pepin Lehalleur (Ref 2) gives the compn as K nitrate 60, Na nitrate 16, sulfur 25 and charcoal 9%

Refs: 1) Daniel (1902), 664 2) Pepin Lehalleur (1935), 287

Pyronite. One of the names for Tetryl (qv)

Pyronitrides. Expls patented in 1880–81 by Prodhomme and examined in 1884 by the Commission Française des Substances Explosives. They contained Na nitrate 35–18, K nitrate 35–45, spent tanbark 15, Na sulfate 2–3, sulfur 6–9, charcoal 3, rosins 4–3, and tar 7%

Refs: 1) Anon, MP 6, 74 (1893) 2) Daniel (1902), 664
Pyronome of DeTret. An inexpensive mining expl patented in Engl in 1859 contg Na nitrate 71.5%, sulfur 13.5%, and charcoal 15% (Refs 1 & 2). A subsequent Pyronome of Salle & Sandoy was patented in Fr in 1881 and contd K nitrate 69%; sulfur, charcoal, metallic Sb & K chlorate 15%; the balance being rye flour contg a small quantity of K dichromate (Ref 1)
Refs: 1) Daniel (1902), 664  2) Pepin LeHalleur (1935), 287

Pyropaper (Pyropapier or Papier Fulminant in Fr). An expl prepd by plunging unglazed paper into a mixt of nitric and sulfuric acids for 2 minutes. After submitting the paper to the usual process of stabilization and drying, it was cut into small pieces and used in primers for needle rifles (fusil à aiguille in Fr) (see in this Vol, N22-R)
Ref: Daniel (1902), 665

Pyrophoric Incendiary Agents. Pyrophoric agents are as a class capable of igniting spontaneously in air. They are often used as igniters of other incendiary agents and to some extent as antipersonnel weapons or as weapons for use against targets contg highly inflammable substances

There are three main types of pyrophoric agents: white phosphorus and other inorganic non metals, finely divided metals, and certain organometallic comds

White Phosphorus (WP). See under Phosphorus (White or Yellow) in this Vol. The most important pyrophoric incendiary agent is WP (Ref 7, p 98). Chevalier in Fr noted the incendiary possibilities of WP in 1789, but it was only used sporadically in warfare until WWI. The first air attacks in WWI by hydrogen-filled dirigibles (Zeppelins) were soon abandoned because P-filled bullets spilled death to lighter-than-air aircraft (Ref 4, p 218). It was used extensively in small arms incendiary bullets and in hand and rifle grenades by all the principle belligerents; the Fr and the Ger used larger cal P shells and the Brit and Americans, trench-mortar bombs

Prentiss (Ref 1) comments on the effects of WP as an antipersonnel agent during WWI:

"When scattered from overhead bursts of grenades and trench-mortar bombs, the phosphorus rained down in flaming particles, which stuck to clothing and could not be brushed off or quenched. The larger particles quickly burned thru clothing and produced painful burns that were slow and difficult to heal. These properties soon became known to troops, and phosphorus was justly dreaded and always caused a demoralizing effect beyond the actual casualties produced"

In the late summer of 1940, Brit airplanes carried NC sheets, 2-inches square and covered with yel P (kept in w prior to release), and dropped them in the region of the Black Forest in Ger. The fire leaves or "visiting cards" did little damage because of cold weather, which often led to slow oxidation rather than to ignition. Similarly, Jap efforts in WWII to do damage by means of small balloons carrying P, which drifted toward the northwestern US coastal region, were ineffectual (Ref 4, p 219)

For many military purposes so-called "plastic white phosphorus" (PWP) is used. The properties are essentially the same as WP. Granules of WP are bound together in a rubbery soln which prevents their breaking up to the same extent when dispersed by an exploding munition. PWP is prepd from a slurry of WP granules in cold w with a viscous soln of synthetic rubber (Ref 7, p 100)

Zirconium. While almost any metal in the finely divided state exhibits pyrophoric properties, a few metals when abraded emit a shower of sparks of sufficient temp to ignite hydrocarbon vapors. Cerium is the best known metal of this kind for commercial purposes, such as gas lighter flints. For military purposes Zr is the most used. It has found applications in HE and armor-piercing incendiary ammo, the lining of shaped-charge rounds, and in incendiary cluster bombs (Ref 7, pp 100–01)

Though the element was discovered in 1789 it was not prepd in the pure state until 1914. It may be prepd commercially by the reaction of zirconium chloride with magnesium (the Kroll process) and other methods. The principle ore is zircon, deposits of which are found in the USA, Australia and Brazil. A number of special properties, such as exceptional resistance to corrosion and a low absorption cross section, have led to the use of Zr or alloys contg Zr, in many
specialized applications in the chemical, nuclear and manufg industries.

For use in munitions Zr may be alloyed with other metals such as Ti and Pb in approx equal proportions. Fine particles of the metals may be mixed and bound in a synthetic rubber compn. To give added durability to this incendiary core it may be surrounded by a similarly bound compn of Fe and Ni carbonate powder (Refs 2 & 4, p 32)

*Depleted Uranium.* In the natural state U is a mix of isotopes from which two, U_{235} and U_{238}, are extracted for use in nuclear reactors and weapons. What remains after the extraction is known as *depleted uranium* which now exists in large quantities and for which few uses have so far been found. One property of U is its high d — it is heavier than Pb — and this has led to the investigation of its military applications.

Pellets, slugs or flechettes made of U have very good powers of penetration. However, U is softer than steel so that in the process of penetrating an armored steel plate it is partially pulverized. Since in this form U is pyrophoric (self-igniting), such projectiles have an incendiary as well as a penetrating effect. According to one account of flechettes made of depleted U:

"... darts penetrate conventional steel plate better than tungsten tipped weapons. The darts also burn as they go through steel plate and spew flames inside the tank" (Ref 8)

In the process of burning, toxic compds are formed, which may produce delayed effects on personnel exposed to the smoke (Ref 7, p 101)

*Triethylaluminum (TEA).* A number of organo-metallic compds are spontaneously inflammable in air. Others, like organosodium and organopotassium compds, are not only spontaneously inflammable in air but react violently with w and carbon dioxide (Ref 4, p 24)

One member of this class of compds, known to be used as an incendiary agent, is triethylaluminum \([\text{Al(C}_2\text{H}_5)_3]\). Similar agents, such as trimethylaluminium or trimethylmagnesium, might also have possible military applications as incendiaries. Diethyl zinc has been employed as an igniter (Ref 3)

Triethylaluminum is a colorl liq which burns with a bright flame reaching temps of up to 2300°, which are comparable to those attained by the metal incendiaries. However, it burns very rapidly and the effects on material are limited. For weapons use it is thickened with polyisobutylene, a very long chain polymer, certain fractions of which are very tacky and are used as adhesives for pressure-sealing tapes. Polyisobutylene-thickened TEA is comparable to napalm in that it has two components: a thickener and an inflammable agent. The term "thickened pyrophoric agent" (TPA) is sometimes used for agents of this kind (Ref 7, p 102)

Production of TPA is much more complex than that of napalm, limiting it to those nations with an advanced petrochemical industry. Because of the reactivity with air, production is usually carried out in an inert atm of nitrogen or helium. Polymerization of isobutylene is also a complex process, requiring catalysts such as Al, Ti or Mo

TEA is currently being used in small incendiary rockets which can be fired from the shoulder by a lightweight launcher, designed to replace conventional flamethrowers. It is the incendiary agent in several prototype large cal incendiary projectiles for use by armored vehicles (Ref 7, p 102)

Expts have shown that if TEA is thickened with only 1% polyisobutylene (instead of the usual 6%) it is possible to produce a chemical fireball which radiates sufficient thermal energy to destroy or damage military targets. It is reported that such a weapon could cause third degree burns on occupants of bunkers within a few seconds, whether or not the agent hit individuals. Previously only nuclear weapons were able to produce damaging levels of thermal radiation (Ref 5)

The concept of the "controlled chemical fireball" is said to have significantly advanced the potential effectiveness of incendiary weapons. Theoretical studies have indicated that a great many applications may be possible, since, by changing the blend of the chemical constituents so as to achieve predetermined rates of combustion, the incendiary agent may be adapted to various operational requirements

In order to permit safe handling and storage, TEA may be made non-pyrophoric by the addition of soluble siluents (for example, n-hexane). "The diluent is expected to flash off when the flame weapon is employed rendering the basic TEA payload pyrophoric again. An effective
delayed, combined flameblast effect should result from the flaming TEA and the deflagrating n-hexane vapor cloud" (Ref 6) 

*Inorganic Substances Which Ignite in Water.*

Na is a very reactive substance which is never found free in nature. It is not generally used as an incendiary agent as such but, because of its tendency not only to float on w, but also to ignite spontaneously in contact with it, it may be added to napalm for use against river targets or enemy positions in rice paddy fields or in snow (Ref 7, p 103 & Ref 4, pp 28–29)

K also has the property of igniting spontaneously in w. The pure metal is more difficult to ignite than is Na. Ba, Ca and Li also ignite in the presence of w, though not as vigorously as Na. Li is the lightest of all metals and has the highest specific heat of any solid. It can burn with a temp of up to 1350°. Li was used for the case of a WWII Jap 70kg P incendiary bomb (Ref 7, p 103)

*New Incendiary Agents.* A great many other substances have been investigated in a search for new incendiary agents. Most interest at the present time seems to be focused on agents which ignite spontaneously, thereby avoiding the need for a fuse. Agents of this kind are particularly suitable for use in small rockets, artillery projectiles and aircraft bomblets which can be distributed over a large area.

In addition to pyrophoric organometallic compds of the TEA type, a number of B compds are pyrophoric, including aluminum borohydride, pentaborane and the B alkyls, such as triethylboron. An alternative means of ensuring spontaneous ignition is to utilize a hypergolic oxidizing agent, that is, an agent which generates so much heat while oxidizing a fuel that the fuel ignites. Agents which are hypergolic with petrol are the interhalogens, chlorine trifluoride, bromine trifluoride, and bromine pentafluoride (Ref 7, p 103)

Many of these substances have been investigated in the context of rocket propulsion technology, since, chemically, the combustion of rocket fuels is related to the combustion of incendiary agents. Though by-products of rocket research may be theoretically of interest as potential incendiary agents, it remains to be seen whether they are feasible economically (Ref 7, p 103)


*Pyro* Powder. A term used for smokeless powder prep'd from Pyrocellulose

**PYROTECHNICS**

**Introduction**

Pyrotechnics is the technology of utilizing exothermic chem reactions when these are, generally speaking, non-expl, relatively slow, self-sustaining and self-contained.

Pyrotechnics is usually distinguished from its sister technologies, expls and proplnts, even though their functions frequently overlap. There has grown up around the sciences of expls and of propulsion such a large body of specific knowledge that the scientific contributions of pyrotechnics are frequently obscured.

Pyrotechnic reactions are employed for the sake of the evolved heat, sound, or smoke; for the generation of high temp, flames, colored light, a working gas or a propagating reaction front. Pyrotechnic devices tend to be storable, compact, and capable of being triggered by a small external force while being in complete isolation from external influences for prolonged periods.

Historically, military pyrotechnics had their origin as incendiaries. The Bible refers to the use of firebrands (Judges 15; 4, 5) and to the action of water on naphtha and burnt lime (II Maccabees; 20–36) (I Kings 18; 31–38). Such self-igniting systems were known as "automatic fire" (Ref 130, p 5) and culminated in Greek Fire (Vol 7, H1 17). Crucial to the further develop-
1) Flares and Signals

Photometry

The inherent complexity of photometry is made greater by the confusion in use and the naming of the earlier units (Ref 134, p 6-17)

Quantities of interest in describing the performance of light are the intensity, I, (candela, cd), the illuminance, E, (lumen/square meter, lm/m²), the light output, C, (lumen/watt, lm/W) and the light efficiency. Intensities of flare combs are detd exptly (MIL-C-18762), and facilities for these measurements are found at all major military arsenals. The illuminance is defined in terms of the height of the burning flare, h, (or the distance from the surface to be illuminated) and the radius of illumination, r, such that (Ref 134, Fig 6-12)

\[ E = 1 \times (i^2 + h^2)^{3/2} \]

The light output per unit energy in terms of the heat of reaction of the flare mix burning in air, Q, having a mass, m in time, t, is (Ref 149, p 232)

\[ C = 4\pi t / Qm \]

A means for describing the volumetric efficiency of a flare is the radiant energy per steradain per unit flare volume (W·sec/ster cm³), the RED (Ref 133, p 227), such that the RED, the burn time of the flare and the curve of the spectral distribution constitute, for most purposes, a full description of a flare.

Flares have modified grey body spectral distributions, although in some current applications the chief interest is in the long wave length components. One method for discarding the visible spectral component (as one would in a decoy) is to burn the flare within a long cylindrical transparent tube in which the inner walls are protected by an air stream. The transparency of the tube is regulated by infrared windows. The second approach requires that a quasi-gasless reaction take place in an enclosed chamber which is coated with a refractory possessing desirable optical properties (Ref 133, pp 223-47). Present developments in electro-optical devices have increased the understanding of the spectral characteristics of flare light. Image intensifiers and low level light television employ photo emitter surfaces which have enhanced performance in the red or near infrared spectral region. The admixture of alkali nitrates other than Na results in light in the near infrared, see Table 1. The ground cover is more reflective in the
infrared than in the visible part of the spectrum so that the apparent lower brightness of the Na-free flares is effectively compensated (Ref 134, Table 4-2).

Table 1

Infrared Flare Formulas (from Ref 121)

<table>
<thead>
<tr>
<th>Component</th>
<th>Wavelength Emitted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.76 μm</td>
</tr>
<tr>
<td>Silicon</td>
<td>10</td>
</tr>
<tr>
<td>KNO₃</td>
<td>70</td>
</tr>
<tr>
<td>CsNO₃</td>
<td>–</td>
</tr>
<tr>
<td>RbNO₃</td>
<td>–</td>
</tr>
<tr>
<td>Hexamethylene</td>
<td>16</td>
</tr>
<tr>
<td>Tetramine</td>
<td>–</td>
</tr>
<tr>
<td>Epoxy Resin</td>
<td>4</td>
</tr>
</tbody>
</table>

Metal oxidizers contribute their energy in the form of spectral emission at characteristic frequencies. The human eye has the greatest sensitivity to the Na emission. For this reason, Mg-Na nitrate flares are selected as the best intensity light source.

Compns for illuminating shells and flares contain 53–58% Mg (MIL-P-14067A), 36–40% Na nitrate (MIL-STD-1233) and 4–8% Laminac binder (alkyd-styrene resin MIL-R-7575A) (Ref 138, pp 357–62). The thermodynamic data for flare compns is given in Ref 134, p 6-38. Further data on illuminating devices and compns is found in Vol 7, I31. The work on providing safer flare formulations is continuing and it was described in Ref 85. A major theoretical analysis of the physical principles of flare performance coupled with an exptl verification program was published by the Aerospace Research Corp (Ref 27).

Signal Formulations

Typical formulations and designs of signal flares are described in Vol 6, F63, and for Star Shells in Vol 7, I32 and Vol 4, D959. The purpose of signals differs from that of flares (illuminants) in that the signal light source must be discriminated from the background illumination. As such signals are generally colored, the problem is enhanced by fog, snow, and rain. The subject of visibility is discussed in Ref 134, p 4-1.

Because signals are generally fired in a prearranged sequence, their deployment is open to imitation by the enemy. By using a combination of spectral components, the color of the flame is different when viewed through a filter than the color of the unfiltered signal. Such a signal compn is given in Table 2 of Ref 105.

Table 2

Red-Green Flare System, Parts by Weight

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Nitrate</td>
<td>30</td>
</tr>
<tr>
<td>Strontium Nitrate</td>
<td>13</td>
</tr>
<tr>
<td>Potassium Perchlorate</td>
<td>9</td>
</tr>
<tr>
<td>Magnesium</td>
<td>30</td>
</tr>
<tr>
<td>Dechlorane</td>
<td>12</td>
</tr>
<tr>
<td>Polyvinyl Acetate Resin</td>
<td>4</td>
</tr>
</tbody>
</table>

Unfiltered, the green and red region combine to produce a yellow color which resembles the color of a pure yellow flare.
A special type of a flare is a thermal decoy which has a strong emission in the infrared. Decoys may utilize the Mg-fluorocarbon reaction which form hot carbon particles as the source of radiant energy (see sample equil calcn, Section 4 of the article) (Ref 59)

Ellern (Ref 138, p 181) also describes pyrotechnic means of producing explosive and whistling sound. Recent advances in the art of generating oscillating light signals are described in Section 8 of this article

2) Colored and White Smoke

Screening Smoke

The pyrotechnic generation of smoke is almost exclusively a military device for screening and signaling. While first encountered on a significant scale in WWI, its importance was not realized until early in WWII when the bulk of the presently known data were collected. In the last 30 years studies of smoke have continued at a reduced rate.

Screening smokes are generally white because black smokes are rarely sufficiently dense. Signal smokes, on the other hand, are colored so as to assure contrast and be distinct in the presence of clouds and ordinary smoke.

Smoke has been found to aid the daytime observance of tracer projectiles and also for tracking space vehicles during launch. Specific smoke tracers for training pilots have been produced (See Section 3 of this article). The 0.50 caliber M48 spotting-tracer was developed specifically to take advantage of the appearance of a smoke puff at the point of impact which persists for a longer time than does the flash.

Whereas smokes are often characterized by the mode of their formation, any condensed suspension of particles ranging from 0.01 to about 5.0 μm can be considered a smoke. These particles, when suspended in air, reflect, scatter and absorb radiation in a complex manner. A comprehensive model of these interactions in terms of visibility under various conditions was described recently (Ref 62).

The following are pyrotechnic methods for smoke generation as opposed to mechanical methods such as atomization of fog oil, of Ti tetrachloride (FM smoke) or of S trioxide.

This discussion is drawn from Ref 134, which should also be consulted for earlier references:

```
a. Venturi Thermal Generator Type

The smoke producing material and the pyrotechnic fuel block required to volatilize the smoke material are in separate compartments. The smoke-producing material is atomized and vaporized in the venturi nozzle by the hot gases formed by the burning of the fuel block.

b. Burning Type

Burning-type smoke compositions are intimate mixtures of chemicals. Smoke is produced from these mixtures by either of two methods. In the first method, a product of combustion forms the smoke or the product reacts with constituents of the atmosphere to form a smoke. In the second method, the heat of combustion of the pyrotechnic serves to volatilize a component of the mixture which then condenses to form the smoke.

c. Explosive Dissemination Type

The smoke producing material is pulverized or atomized and then vaporized, or a preground solid is dispersed by the explosion of a bursting charge.

An important example of the first type is the oil smoke pot which is powered by a slow burning, gassy pyrotechnic mix such as amm nitrate and amm chloride with a small amount of carbonaceous fuel. The resulting gas jet pulls a stream of oil from a reservoir and injects it into a venturi where the formation of the aerosol takes place.

White P, either in bulk or in soln, is a good example of the burning type of smoke generator. The resulting colloidal suspension of P pentoxide is quickly hydrolyzed by moisture to become phosphoric acid droplets which are the actual visible constituent of the smoke. Various other burning type smoke generators exist such as those used for signaling purposes and which use red P, metallic phosphides, or P trichloride as the source of the particulate cloud.

Another important burning type of smoke generator is the HC smoke mix which has been prepd with a number of combinations of Zn with a chlorine carrier to form, on combustion, Zn chloride. For example,

2Al+C_2Cl_6+3ZnO → Al_2O_3+2C+3ZnCl_2

HC mixts are used in the AM-M8 Smoke Hand Grenades, in the HC floating smoke pot (M4A2) and in the M1 Smoke Canister.

The expl dissemination type of smoke gene-
```
rator may contain metallic chlorides which upon dispersal hydrolyze in air. Examples are Ti,
Si, and stannic tetrachloride. An effective smoke agent, whether it be mechanically dispersed
from an aircraft spray tank or vaporized thermally, is a mix of S trioxide and chlorosulfonic
acid (FS smoke agent) which upon hydrolysis forms sulfuric and hydrochloric acid dispersions.
Of course, all such formulations are highly corrosive, and, if not outright toxic, then con-
ducive to pulmonary edema

The so-called “standard smoke” is a smoke of
such a density that a light of 25 cd intensity is
just invisible when observed thru a layer of
approx 30 meters. The amount of smoke agents
required to produce one cubic meter of standard
smoke is given in Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>g/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>White Phosphorus</td>
<td>0.064</td>
</tr>
<tr>
<td>Sulfur Trioxide</td>
<td>0.099</td>
</tr>
<tr>
<td>FS agent</td>
<td>0.116</td>
</tr>
<tr>
<td>HC Mixture</td>
<td>0.127</td>
</tr>
<tr>
<td>FM agent</td>
<td>0.159</td>
</tr>
<tr>
<td>Crude Oil</td>
<td>2.11</td>
</tr>
</tbody>
</table>

ably melting points below 150° and be stable
in the vapor phase. The following are currently
used dyes:
Orange: 1-(4-Phenylazo)-2-naphthol
Yellow: N,N-Dimethyl-p-phenylazoaniline
Blue: 1,4-Diaminomacanthraquinone
Mixes of these dyes produce muddy colors of
various hues

Lastly, dyes can be dispersed by expl charges.
These generate colored clouds (about 10x20m)
which are formed instantaneously and which
have a life expectancy, depending on environ-
mental conditions, from 65–85 seconds, whereas
aerial burning of the aforementioned burning
type produces streamers about one meter across
and which last for about 57–120 seconds

3) Tracers and Fumers

The principle small arms application of
military pyrotechnics is in tracer munitions,
where they serve as incendiaries, spotters and as
fire control. A thorough review of tracer munition
design was prepared by Frankford Arsenal
(Ref 33)

Tracer munitions are the most effective means
of fire control for rapid firing small arms. When
used in machine guns, they are belted in a pre-
determined sequence, depending on the mission,
with ball rounds, incendiary rounds or armor-
piercing rounds. More recently, the trend in
20–30mm rounds has been to accommodate
combined armor-piercing–incendiary–tracer
functions which has resulted in every round
being a tracer

Historically, storability, ignitability and burn
time have been recurring problems in tracer
munition fabrication. The endothermic de-
compositional nature of organic oxidizers and the brief
exposure to the propellant flame (0.5–2msec)
brought about the need for special igniters and
subigniters. Furthermore, the desire to hide the position of the gun at night by delaying the ignition for a short distance from the muzzle, caused the development of dim igniters. The mechanism of tracer reactions is a complex one as the burning rate and the brightness of the trace increases with spin rate of the bullet, but decreases with altitude. The reaction equilibria were examined (Ref 90) and it was found that the solid phase is principally Mg oxide, the Sr oxide being converted to the volatile chloride by the action of PVC. Hence, the color strengthening chlorinated additives function by volatilizing the spectrally active compd. The reaction products are mainly gaseous, being rich in Mg vapor and CO. The trace brightness originates therefore in the plume reaction. Attempts at minimizing the side visibility of the plume by using gasless reactions have also reduced the trace visibility (Ref 82). Comps for use with electrooptical devices have also been developed (Ref 40). These compns consist of Ca resinate, Ba and Sr peroxides and Mg carbonate.

The color of tracers is not judged by a numerical color value but on the basis of visual observation in daylight and at night. Acceptance is based on visibility over a range of 1000m for 5.56 and 7.62mm and up to 2500m for 20mm rounds. Red tracers are more visible to the human eye as longer light waves penetrate haze, dust and fog better, and hence these are most commonly used. The Vietnamese are said to have used green tracers so that in addition to providing fire control, the tracers helped identify the combatants in night-time encounters.

The compn of tracer mixts used in the United Kingdom, as well as a discussion of their burning characteristics in spinning projectiles, is given in Ref 81. A good review of the USSR developments in tracer technology is given by Shidlovski (Ref 149, p 303). Ellern (Ref 138, p 362) lists the compn of artillery tracers. With the trend toward smaller caliber ammo for hand held weapons, the loading of miniature tracer cavities became difficult. For instance, the XM216 is a dart-like finned projectile (flechette) with a 1.52mm diameter opening and 15.9mm cavity depth. The charging problem was overcome with Visacore (Refs 20 & 52), a mixt of 65% 23 μm Zr, 30% K perchlorate and 2–5% vinyl alcohol acetate resin (VAAR), blended in ethyl acetate solvent. This mixt is swaged in a Pb tube to the desired diameter, and inserted into the tracer cavity, trimmed and consolidated. A tracer formulation for external application to sabot type projectiles was recently patented (Ref 114). These rely on sintered depleted U and Ni powder and provide a trace of 2000m visibility.

Hy-pergolic reaction systems have been proposed (Refs 46 & 73) for 5.56mm ammo, specifically triethylaluminum (TEA) together with inorganic oxidizers. This system is self-igniting in air, but is compatible with some nitrates, chlorates and perchlorates.

A recent development is the use of gas generating tracers ("fumers") for base drag reduction (Refs 74, 75 & 84). The base drag develops because a partial vacuum is created behind a moving projectile, causing a ballistic mismatch between tracer and ball rounds. Fumers utilize the gaseous products of a burning tracer, resulting in increased range and decreased time of flight. A logical extension of the fumer concept is a rocket assisted bullet which would have the advantage of a flat trajectory, min recoil and max velocity at impact. Such small arms rockets with as little as 3mm diameters and 35mm lengths, having foil wrapped casings, perforated double-base proplnt grains and a thermite igniter, have been developed as an anti personnel weapon (Ref 39).

Extension of the visible range for 20mm rounds to ranges beyond 2500m has been made possible by the folded cavity tracer capsule (Ref 102) which is illustrated in Fig 1. The folded cavity is designed to function as follows: the propplant gases ignite the igniter charge as in all tracer ammo; then, the igniter material ignites the initial tracer charge in the central cavity. As the flame front reaches the bottom of the central cavity, it transfers to the annular cavity containing the downrange tracer charge. As this charge burns, the central (Al) column melts partially or totally, contributing increased fuel to the process. The concept is said to work with any tracer compn, although those which are rich in PVC are favored (see Table 5).

Other uses of tracer rounds have been to initiate a self-destruct charge (Vol 7, 110) which prevents unexploded antiaircraft shells from falling to the ground. A recent development introduced the inclusion of oxamide to slow the
Whereas generally U is considered to be an incendiary fragment generator, one patent was issued for the inclusion of about 50% depleted U with such oxidizers as KClO₄, Ba(NO₃)₂ or NH₄NO₃ (Ref 17) for use in spotting rifle projectiles.

4) Incendiaries

The history of incendiaries and incendiary projectiles thru WWII was reviewed earlier (Vol 7, 165). The principal advances in the intervening years have been in the wider use of metals which are known to yield pyrophoric fragments, in the fabrication of incendiary bombs, and in the use of Zr, Ti and mischmetal. Early small arms incendiary mixts are reviewed in Ref 134, Table 5-7. As a pyrotechnic metal, Zr has become available only in the last two decades as an intermediate component of nuclear reactor development. The metallic form of interest to pyrotechnics is the sponge which is easily pulverized and which is possessed of a high surface area. Compacted sponge is preferable to wrought metal as it forms incendiary fragments more easily (Ref 128).

The characteristics of a metal which contribute to a good incendiary capability are not yet fully understood nor have they been completely defined. Hillstrom (Ref 64) found that pyrophoricity is related to the ratio of the oxide volume to the metal volume, a ratio above one giving rise to the "popcorning" effect which is

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**Table 5**

Typical Formulas for Igniter and Tracer Compositions (from Ref 33)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Delay Action Igniter, I-136</th>
<th>Dim Igniter, I-194</th>
<th>Daylight (Bright) Igniter, I-276</th>
<th>Red Tracer R-257</th>
<th>Fumer (Ref 75 R-284)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium Peroxide</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>-</td>
<td>6</td>
<td>15</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>I-136 Igniter</td>
<td>-</td>
<td>94</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcium Resinate</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Barium Peroxide</td>
<td>-</td>
<td>-</td>
<td>83</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zinc Stearate</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Toluidine Red (Identifier)</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Strontium Nitrate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>Strontium Oxalate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Potassium Perchlorate</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Polyvinyl Chloride</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
</tbody>
</table>
### Table 6
Properties of Pyrophoric Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta F$, kJ/mol O</th>
<th>Oxide Vol/Metal Vol</th>
<th>Electronic Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>−536</td>
<td>3.10</td>
<td>$6d^1 7s^1$</td>
</tr>
<tr>
<td>Th</td>
<td>−587</td>
<td>1.36</td>
<td>$6d^2 7s^2$</td>
</tr>
<tr>
<td>Zr</td>
<td>−512</td>
<td>1.55</td>
<td>$4d^2 5s^2$</td>
</tr>
<tr>
<td>Hf</td>
<td>−577</td>
<td>1.62</td>
<td>$5d^2 6s^2$</td>
</tr>
<tr>
<td>Ce</td>
<td>−486</td>
<td>1.23</td>
<td>$5d^0 6s^2$</td>
</tr>
<tr>
<td>La</td>
<td>−641</td>
<td>1.11</td>
<td>$5d^1 6s^2$</td>
</tr>
<tr>
<td>Pr</td>
<td>−621</td>
<td>1.12</td>
<td>$5d^0 6s^2$</td>
</tr>
<tr>
<td>Nd</td>
<td>−617</td>
<td>1.12</td>
<td>$5d^0 6s^2$</td>
</tr>
<tr>
<td>Sm</td>
<td>−431</td>
<td>1.06</td>
<td>$5d^0 6s^2$</td>
</tr>
<tr>
<td>Y</td>
<td>−427</td>
<td>1.44</td>
<td>$4d^1 5s^2$</td>
</tr>
<tr>
<td>Ti</td>
<td>−426</td>
<td>1.78</td>
<td>$3d^2 4s^2$</td>
</tr>
<tr>
<td>Be</td>
<td>−582</td>
<td>2.77</td>
<td>$- 2s^2$</td>
</tr>
<tr>
<td>Al</td>
<td>−526</td>
<td>1.28</td>
<td>$- 3p^1$</td>
</tr>
</tbody>
</table>

thought to aid in the self-propagation of oxidation. Furthermore, the free energy of the oxide formation (per unit oxygen atom) should exceed 400kJ/mole O. Some elements, such as Al and Be, possess these desired properties but in fact fail to burn spontaneously except as fine powders. For such boundary line cases the electronic structure (see below) may play a deciding role. Table 6 lists these properties of the best candidates.

The design characteristics, reaction modeling, target simulation and thermodynamic parameters are exhaustively reviewed in a four volume study by the Denver Research Institute (Ref 129).

A variant ignition mechanism, based on shock compression along a Hugoniott curve, was proposed as a source of the ignition energy (Ref 76). Distended metals in the form of powders and sponge are seen to be of particular pyrophoric value, not only because of their high degree of dispersion, but because relief of pressure behind a shockwave passing thru compressed powder creates a persistent hot zone, so as to promote their ignition.

Pyrophoric elements are characterized additionally by largely unfilled d shells. Certain alloys spark particularly well when alloyed, as for example, ZrSn and FeCe. It appears that those alloys spark best which are eutectics, and in which the compn is rich in the pyrophoric element, but that such pyrophoricity is lost when the alloying agent forms an intermetallic compd, even though compd formation is accompanied by increased fragibility. Compds do not have electrons in the conduction band, and the change in pyrophoricity may be connected therewith.

Pyrophoric penetrators equal in effectiveness to those containing U are reportedly provided by those containing spark sintered bodies of 49–95% W, 4–50% Zr and a binder of ductile metal such as Ni, Fe, Co or Cu (Ref 115). Even though U is the most pyrophoric of all elements, it is not expected to see use as an incendiary because of its toxicity and its great value as a nuclear fuel.

Incendiary munitions for use against supersonic aircraft require rapid initiation of long burning incendiary fragments. Whereas this problem has never been solved in a satisfactory manner, coarse particles (20–60 mesh) of Zr sponge are known to ignite on impact and to burn about 300msec. Less dense and more inexpensive Ti will only initiate when the fragments are substantially smaller than 60 mesh, only to burn too quickly (Ref 129, p 317). The data comparing the performance of Ti and Zr tend to be contradictory because the degree of purity of the metals is rarely specified. Several methods are known for initiating coarse (20–60 mesh) Ti sponge which then will burn for up to
300msec. One method consists of admixing 25% K perchlorate, 25% Al—Mg alloy and 50% coarse Ti sponge (Ref 19), resulting in a burst duration of 275msec. Alternately, one may compound the coarse Ti sponge with Teflon or a similar fluorocarbon, which ignite when subjected to shock (Ref 76). The development of fluorocarbons as oxidizers has been one of the principle new developments since WWII, prompting extensive theoretical and expd work. The volumetric heats of reaction of pyrophoric elements with fluorocarbons are listed in Table 7.

Table 7
Maximum Volumetric Heats of Reaction for Metals Reacting with Fluorocarbons (from Ref 8)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Product</th>
<th>kJ/cm³ (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>BeF₂</td>
<td>-24.0</td>
</tr>
<tr>
<td>La</td>
<td>LaF₃</td>
<td>-21.0</td>
</tr>
<tr>
<td>U</td>
<td>UF₃</td>
<td>-19.8</td>
</tr>
<tr>
<td>Mg</td>
<td>MgF₂</td>
<td>-19.8</td>
</tr>
<tr>
<td>Hf</td>
<td>HfF₃</td>
<td>-19.0</td>
</tr>
<tr>
<td>U</td>
<td>UF₄</td>
<td>-18.9</td>
</tr>
<tr>
<td>Zr</td>
<td>ZrF₃</td>
<td>-18.6</td>
</tr>
<tr>
<td>Zr</td>
<td>ZrF₄</td>
<td>-18.6</td>
</tr>
<tr>
<td>Hf</td>
<td>HfF₄</td>
<td>-18.2</td>
</tr>
<tr>
<td>Ti</td>
<td>TiF₃</td>
<td>-17.0</td>
</tr>
<tr>
<td>Ti</td>
<td>TiF₄</td>
<td>-14.6</td>
</tr>
</tbody>
</table>

(*) The numerical values are strongly affected by the stoichiometry and by the effective densities of the reactants.

Enhancement of reactivity of incendiary components has been claimed by the introduction of impurity states, particularly into metallic oxides (Refs 56 & 86). Impurity states have a twofold effect: they disturb the lattice structure of the oxide (and so increase the diffusivity of the reactants), and they disturb the electronic distribution on the surface as well as in the bulk. The argument is made that by “doping” the oxide, or by controlling the formation temp, one may change an oxide from an n-type to a p-type semiconductor and hence cause it to become a better electron acceptor, and vice versa.

A promising discovery for increasing the ignitability of Thermite (Vol 7, 173-R & Ref 134, pp 3–5) mixes has been the admixture of Ni powder (Ref 29). The basis for this finding is the highly exothermic formation of the intermetallic compd NiAl, which proceeds progressively after ignition at 650° (Refs 45 & 68).

The theoretical study of incendiary reactions has been aided by the use of computer programs for the study of the equil products (Refs 15 & 41), as well as for the prediction of the adiabatic reaction temps. An example of the complexity of the reaction products of a fluorocarbon, compounded with 5% epoxy binder, is given by Tanner (Ref 80). It will be observed, that only the carbon remains as solid product, and that the effect of the fluorine is one of increasing the fraction of gaseous products, as well as to provide the thermal energy (see Table 8).

Table 8
Equilibrium Composition of the Product of the Reaction of Magnesium with a Fluorocarbon at 1200 K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>C(s)</th>
<th>C₂N</th>
<th>C₃</th>
<th>MgF</th>
<th>MgF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(s)</td>
<td>0.45316</td>
<td>0.00118</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.00078</td>
<td>0.03023</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>0.00755</td>
<td>0.00485</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF₂</td>
<td>0.00206</td>
<td>0.03197</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>0.00224</td>
<td>0.44743</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂N</td>
<td>0.00118</td>
<td>0.01115</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adiabatic Reaction Temperature: 3400 K

5) Delays and Fuses

A delay element is a self-contained pyrotechnic device consisting of an initiator, delay column and an output charge or relay, all assembled into a specially designed inert housing. It provides a predetermined interval between initiation and functioning of a device.

Delay elements have been described earlier (Vol 3, D50 & Vol 4, D863 & D872). Work on delay systems continues because the existing delay mixtures do not store well, and scale-up is not as flexible and as precise as is desired. A basic reason is that gasless delay mixts are not truly gasless in that gaseous reagents are present in the flame front or in the ignition mix which contribute to the pressure in the column (Ref 32), so that the burn time is not strictly a linear function of the column length. Some workers have called this phenomenon the “anticipatory effect” (Ref 10 & Ref 134, Table 5-17, 18).

The almost universal chromate oxidizers are claimed to be carcinogenic (Ref 67) for which...
the manufacturers desire substitutes. The aging problem is known to reside with the metallic fuel (Refs 21 & 60) which tends to corrode in the presence of moisture. The evidence is conflicting whether protective coating or selection of dry components affords the best solution (Ref 51). It appears that the corrosive effect of moisture is in part compensated by the inhibiting effect of the chromate such that in the case of Mn mixtxs, the burn time stabilizes after an initial increase. Gorbunov (Ref 116) studied many non-toxic, non-corrosive systems over pressure ranges of 1-100 atm, and finds that the burning rates of Na nitrate and carbonate, and K carbonate and sulfate are independent of pressure when reacting with Mg. Intermetallic reaction systems, chiefly Ti–B and Ni–Al, have been studied in recent years (Refs 68 & 106). Reasons for the instability of gasless reactions have been ascribed to "oscillatory burning" (Refs 1, 44 & 107).

A significant discovery was a new commercial product, Pyrofuze (Ref 5 & this Voi) which consists of very thin clad sheets of Pd (or Pt) on Al, or very finely swaged Pd wires which have an Al core. Attempts to incorporate Pyrofuze in delays have met with limited success (Ref 30). Reasons for this have been analyzed (Ref 120) and are ascribed to adverse heat transfer phenomena.

The historical developments in delay formulations have been traced by G. Weingarten (Ref 133, p 254), who also tabulated a wealth of performance data.

The interest continues in accurate delay compns for use at high altitudes and at extreme temps. Ternary compn diagrams of Ba and Pb chromates with B, Mg, Ti, Ta and Nb, all as function of burn time, have been published (Ref 36) as have burn times with Zr–Ni alloys (Ref 49). Over large ranges of proportions these systems are excessively gassy. An important system is one employing W, Mo or Cr together with perchlorates (Ref 7). These mixts have a wide range of burn times, depending on the compn, but tend to be gassy. Problems related to the variability in delay train performance have been addressed by Valenta (Ref 58).

As propagation rates of gassy reactions are pressure dependent, so are gasless reactions temp dependent. This temp dependence has been ascribed to the effect of temp on the diffusion rate in the solid phase (Ref 66) or to classic kinetic parameters (Ref 47), but no satisfactory method for compensating for the temp effect has been found. The usual approach is one of raising the temp of the reaction (Refs 5 & 89) so as to reduce the percentage change of the exponential term in the Arrhenius expression.

An interesting finding was that diatomaceous earth (SiO2) has a stabilizing effect on the aging characteristics (Ref 60) and an accelerating effect on Ba chromate containing mixts which may be due to the lowering of the decomp temp of Ba compounds by SiO2 (Ref 26).

Improvement in the precision of delay trains is claimed by the use of swaged cords as opposed to pressed columns (Refs 18 & 55), provided that such cords are reasonably long. Another approach consisted of placing a number of delay columns in parallel so as to decrease the spread of the burn times (Ref 22).

Ellem (Ref 138, p 197) has reviewed the theory and technology of pyrotechnic and non-pyrotechnic delay trains, and he stresses problems in obtaining precise long delays in obturated systems and pressure sensitive (vented) systems, while listing the advantages of pyrotechnic delays in terms of reliability and cost. Non-pyrotechnic systems rely on the corrosion or dissolution of a restraint by acid or by a solvent, causing a spring loaded pin to strike a primer or an electric switch to be functional (Ref 138, p 210).

A recent review relating the pyrotechnic reaction mechanism, particle size, stoichiometry, temp and compaction density to burning rate is Ref 66, and a study of the effect of multidimensional heat transfer on the rate of flame propagation is Ref 120, which showed that the material of the delay body has an effect on the performance of most delay compns, a finding which agrees with test data.

Statistical controls in testing delay compns are described in Refs 2 & 152.

Table 9 lists the chief performance characteristics of the most important delay compns. In general, the burn time is controlled within the stated limits by adjustment of the fuel fraction. Other variables are the particle size of the fuel and the presence of additives such as Pb chromate, silica and Viton. Many perchlorate containing mixts are friction and spark sensitive,
<table>
<thead>
<tr>
<th>Delays:</th>
<th>Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-15</td>
<td>1989-1980 ZI-N</td>
</tr>
</tbody>
</table>
| 0-38 | MK-79M-2F/ZI-Nl-
| 0-06 | NAVA |
explaining the intended role of Viton and similar additives in reducing sensitivity

6) Photoflash Compositions

Photoflash powders are loose mixts of powdered oxidizers such as Ba nitrate and K perchlorates with metallic fuels, principally Mg, Al and Zr. These ingredients have such small particle sizes that they burn with expl violence for durations of less than 0.1 sec. At present photoflash powders are used exclusively in military aerial photography, whereas civilian applications are served by electrically ignited Zr or Hf wire containing flashbulbs. Since 1970, non-electric, pyrotechnically functioned, flash cubes have appeared on the market (USPs 3535063, 3540813 & 3674411).

Photoflash bombs and cartridges are pyrotechnic items which are classified with bombs (Vol 2, B229) because of their explosive effect. The various devices are similar, differing principally in size and the amount of delay. When fired, each photoflash cartridge, after 1, 2, or 4 seconds, produces a flash having a peak intensity of approx. 50 million cd with a total output of 5 million cd-sec, whereas photoflash bombs generate above 5 x 10^9 cd.

The literature on flash comps is particularly voluminous, giving rise to the need of correlating or predicting their performance. Comprehensive studies since WWII have shown that Al and Mg are the best fuels at sea level (Ref 134, p 6.62). While atomized Mg gives higher intensities in consolidated comps, atomized Al performs better in loose comps than do other fuels. K perchlorate produces the highest heat of reaction with atomized Al. The output is highest for fuel rich comps and alkaline earth nitrates which are far superior to alkali metal nitrates. Constant Al particle sizes of 22±8μm resulted in optimum efficiency (cd sec/g) at all altitudes. At high altitudes, Zr performs better.

Photoflash comps containing Hf and K perchlorate possess greater luminous efficiency on a volume basis than do other formulations (Ref 128). Zr, for example, when burned in oxygen has an average color temp of 4883°K compared with 5235°K for Hf when measured at peak intensity (Ref 65). In pyrotechnic flash units, substitution of Al with Hf and Ti produced comparable peak output, but inferior output when Zr and Ce were substituted (Ref 37).

Little work is known to have been done otherwise in the last decade on photoflash comps, which continue to be the single most hazardous class of pyrotechnic mixts, both because of the expl character of its combustion and because of the large quantity deployed in any one device. Current emphasis at PicArsn is on improving the handling safety of the powder. A significant engineering advance consisted in the elimination of the preblending step thru layering the separate components within the bomb, followed by vibrating and tumbling as the means of blending (Ref 12).

Typical photoflash comps as well as some of their performance data and device specifications are given in Ref 134, Tables 6-16 to 6-25.

7) Igniters and Initiators

The many aspects of ignition and igniters have been widely covered in this Encyclopedia (Vol 7, 15-R to 19-R). The igniters given in Vol 4, D774-L for tracer munitions are no longer correct (the current comps are given in Section 3 of this article); moreover, the wording “barium oxide” should read “barium peroxide”. Igniters for incendiary bombs are reported in Vol 4, D1016-R and for rim fire ignition on page D1053-R. The description for dim igniters on page D774-L is likewise no longer valid, having been superseded by the mixt described in Table 5 of this article. Typical initiation mixts for expls are listed by their Chemical Abstract ref number in Vol 7, I17. The problem of prime ignition was reviewed in Vol 4, D758 with listings of match comps on pp D760–D761, of BikP&rs on D763, of starting mixts on D764, of ignition mixts on D766, and first fires on D767. Additional systems are described by Ellern (Ref 138, pp 189–96), Shidlovsky (Ref 149, pp 463–73), and Robertson (Ref 139).

A major review of air and water activated (ie, self-igniting) systems was also published (Ref 24).

A special category of ignition system is the cartridge actuated device (CAD) also known as the Propellant Actuated Device (PAD) which serves to generate the mechanical force to close switches (in the manner of a squib) or to perform otherwise mechanical work (Vol 2, C70-R & Ref 138, p I67).

The development of ignition systems is one
of tailoring static, shock, and temp sensitivity to the allowable ignition delay, high altitude ignitability and compatibility. As with other pyrotechnic devices, new ignition systems are constantly being developed to meet specific tasks. Examples of such developments are fluidic expl initiators (Vol 6, F111-R & Refs 57, 103 & 111), exploding bridgewires (Vol 6, E353-R), laser energized expl devices (Vol 7, 1.5), ignition of intermetallic and gasless reaction mixes (Refs 48 & 78), spontaneous ignition kits (Ref 25), as well as the synthesis of coordination compounds to take the place of temp sensitive primary expls (Ref 77).

Ignition mixes of lower static sensitivity have been prepared from Ti hydride and K perchlorate (Refs 117 & 123). It was found that the hydride tends to react with the perchlorate at elevated temps and that such a reaction is progressive, particularly with high hydride concns. No data have been found on Zr hydride mixes, but it is expected that the behavior will be similar. It seems, however, that performance variations are common in Zr mixes, but that these can usually be traced to hydride contamination in the Zr, and that such problems can be solved by heating the Zr in vacuum at about 200°C (Ref 128).

The pyrotechnic literature does not contain a critical evaluation of the ignition response time of primary initiators in terms of their compn, temp tolerance and shock sensitivity. In general, primary expls such as Pb azide or stphnate are selected whenever a brief (microsecond) response is desired, while, for instance, Pb thiocyanate-chlorate mixes are selected when high temps and high radiation environments are encountered, and presumably a longer ignition delay is the price which is paid for the extra margin of safety.

The military practice is one of preference for the stphnate-based types, even though for pyrotechnic applications they tend to be brisant. When in about 1960 the requirement for high temp resistant primary compns (1000 hrs at 37°C) was established, the G 11 type mixes were developed. These mixes are desensitized by a humid environment and are much less sensitive than the stphnate compns so as to require increased firing energy. The brisance is comparable with Pb stphnate mixes. Table 10 lists the composition of the most important percussive primers, while Table 11 compares the characteristics of the formulations based on a report by Lake (Ref 31).

Table 10

<table>
<thead>
<tr>
<th>Component</th>
<th>FA-70</th>
<th>PA-101</th>
<th>G-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Stphnate</td>
<td>—</td>
<td>53</td>
<td>—</td>
</tr>
<tr>
<td>Barium Nitrate</td>
<td>—</td>
<td>22</td>
<td>—</td>
</tr>
<tr>
<td>Potassium Chlorate</td>
<td>53</td>
<td>—</td>
<td>53</td>
</tr>
<tr>
<td>Antimony Sulfide</td>
<td>17</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Calcium Silicide</td>
<td>—</td>
<td>—</td>
<td>12</td>
</tr>
<tr>
<td>TACOT (*)</td>
<td>—</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>Lead Thiocyanate</td>
<td>25</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>TNT</td>
<td>5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Aluminum</td>
<td>—</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>Tetracene</td>
<td>—</td>
<td>5</td>
<td>—</td>
</tr>
</tbody>
</table>

(*) A proprietary secondary expl by DuPont de Nemours & Co

Whereas once BlkPrd was the universal propellant expl, today it finds application chiefly as an igniter. The annual military procurement in the US in 1968 was about 3000 tons, reflecting the requirements of the Vietnamese war, whereas in 1976 consumption dropped to less than 500 tons (Ref 42). Civilian applications

Table 11

<table>
<thead>
<tr>
<th>Primer Mix</th>
<th>Max Continuous Temperature</th>
<th>Rel Primer</th>
<th>Firing Sensitivity (Drop Height ±5%) x Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiocyanate/Chlorate</td>
<td>70°C</td>
<td>soft</td>
<td>1.53 kg-cm</td>
</tr>
<tr>
<td>Stphnate/Chlorate</td>
<td>95°C</td>
<td>brisant</td>
<td>1.98 kg-cm</td>
</tr>
<tr>
<td>G-11</td>
<td>200°C</td>
<td>brisant</td>
<td>6.86 kg-cm</td>
</tr>
</tbody>
</table>
in fireworks, muzzleloading weapons and as a propellant in model rocketry consume another 500 tons of domestic production, although the amount derived from imports is many times this figure. Recently the allowable quantities of BlkPdr which may be stored in a home without a permit has been increased to 50 lbs (22.7 kg) (Title XI, Public Law 91-452)

The US Army is the primary consumer of BlkPdr in the US where it is used as an igniter in flash tubes for artillery shells (Vol 4, D775-R) above 40mm, where besides being effective as a flash reducer it is known to be a better igniter for smokeless powder than the smokeless powder itself (Ref 110). Minor uses of BlkPdr are as a propellant/igniter in flare and smoke cartridge ejection systems (Vol 4, D959), as a delay element (D857) and as an incendiary igniter (D942)

Numerous accidents, coupled with decreased consumption of BlkPdr reduced the domestic US sources to one. Consequently, the US Army has contracted to build a fully automated plant which employs the novel Loevold process (see below), which uses high velocity air to break up and blend the ingredients (Refs 53 & 63). This remotely controlled process is claimed to be safe (Ref 95). The product is to meet US military specifications (Ref 79), although this remains to be demonstrated

The traditional (batch) milling process, essentially unchanged in centuries, grinds the raw material in a wheel mill for many hours, causing pulverization and intimate contact of one component with the other. The resulting mix is pressed, granulated ("corned"), dried, polished and glazed. In the new Loevold process the raw mix is injected as a continuous stream into a jet mill, shown schematically in Fig 2, where collision of particles causes pulverization to < 15 µm, as according to Loevold (Ref 95) the fine particle size provides assurance of close particle contact and equivalence in performance with the mill process powder. The resulting raw powder is then pressed, granulated, glazed and screened as before. Another jet mill process for the fabrication of BlkPdr was patented recently (Ref 108)

From the dimmest past to the present, BlkPdr (Vol 2, B165-R) has been the subject of prolific scientific work, the earlier part of which was reviewed by Urbański (Ref 14). Recent studies dealt with the role of S in lowering the pressure limit of BlkPdr ignition, as well as the profound effect of charcoal volatiles content on the performance (Refs 3 & 109). Description of BlkPdr is frequently in terms of the burning rate, which depends on whether it was measured on loose powder or on compressed, single grains. Confined loose powders burn in a manner which can be described as a low order detonation, velocities of 170m/sec for coarse powders (Ref 70) to 950m/sec for fine powder (Ref 9), and 1500m/sec for sulfurless powder having been reported (Ref 9). A more meaningful criterion is the relative quickness, or the rate of pressure rise as determined in a constant volume bomb (Ref 109)

When BlkPdr is used as a pressed grain, surface normal burning rates can be defined. These studies continue as an important tool in examining the complexities of the burning mechanism. These and other properties of various BlkPdrs have been compared (Ref 72), as has the temp dependence of the burning rates. The enormous volume of published data deals, however, only with conventional, mill process, powder, while the corresponding data on the jet mill powder await the completion of ongoing studies

A new replica BlkPdr is Pyrodex (Ref 110) which, containing 6% sulfur, 10% charcoal, 83% K nitrate and 1% Ca carbonate, has an ignition temp above 260° compared with an ignition temp of 125° for BlkPdr and 135° for smokeless powder
8) Advances in Pyrotechnics

Computer Applications in Pyrotechnics

Since 1968 the availability of theoretical cains from optical spectra, the results of mass spectrometer studies of volatile species and computer programs for the study of high temp equilibria (Refs 15 & 41) has made possible the analysis of complex pyrotechnic reactions. Such techniques will see expanded use in the examination of the spectral characteristics of signals and flares (Ref 80), although prediction of kinetically controlled reaction rates and ignition energies await further mechanistic studies.

For much of the last two decades the science of shock physics was applied to thermomechanical effects in expls (Refs 118 & 147) and proplnts. The further extension of such studies to pyrotechnics (Ref 76) may provide further insights into the functioning of improved incendiary munitions by multidimensional analysis of wave propagation into distended matter (Refs 135 & 151). Similarly, propagation rates and ignition energies in condensed phase reactions have also been modeled (Refs 66, 78 & 120).

Application of Solid State Physics to Pyrotechnics

Modification of the reactivity of metallic oxides by doping (Refs 56, 86 & 96) may result in safer igniters, initiators and reaction mixts. In devices which can tolerate moderate ignition delay, further development of non-primary initiators (Refs 31, 77, 97 & 112) will extend the storability, the manufacturing safety, the electromagnetic field and spark sensitivity and the high temp compatibility of pyrotechnic devices.

Pyrotechnic Laser Technology

It is not surprising that the reliability, portability and rapid energy release of pyrotechnic systems should have suggested their use in laser technology, both as light source for pumping and as the source for the inversion population. It was realized that pyrotechnic laser devices might be inexpensive single shot laser weapons. Stokes and Steng (Ref 16) suggested the burning of cyanogen as the light source for pumping Nd and ruby lasers, whereas Kaminskii and Bodretsova (Ref 23) studied KClO₄ and Zr flash compns. A recent review discusses the feasibility of using the shock driven CS₂ + O₂ reaction for use in a gas dynamic laser (Ref 162).

Although no operating data were found on pyrotechnic gas dynamic lasers, Douda (Ref 43) explored some of the theoretical requirements. Of the systems which he considered (principally flare compns), the alkaline earth lasers are the most interesting in that the MOH and MCl radicals are removed from their ground state by further chemical reaction to the bivalent molecule. The concn of the transient species is, as reported (Ref 90), a strong function of temp, suggesting that a possible lasing action could be achieved by "freezing" of radicals thru adiabatic expansion. If a direct inversion does not occur, the species may have to be pumped using possibly nitrogen and nitric oxide. Both molecules are capable of being excited vibrationally to an energy level which is nearly resonant with the excited levels of MOH or MCI where M is either Ba or Sr. The above schemes await exptl verification.

Electromagnetic Field Effects

The initiation characteristics of primary expls have profound implications for the storage and functioning of pyrotechnic devices. Specifically, the sensitivity to static electrical discharges and to the presence of RF electrical fields is many orders of magnitude greater in terms of energy required to initiate (Vol 5, E43) than if the same initiation were to take place thermally or by shock initiation of thin wafers (Ref 118). Significant advances have taken place in the study of this phenomenon. H.D. Fair and D.S. Downs at PicArsn have shown that electronic processes can be used to achieve direct non-thermal initiation of both primary and secondary expls (Ref 87). The electronic energy levels in expls were determined by low temp optical absorption techniques and the electronic transport properties were obtained by photoconduction and related solid state measurements (Ref 71). The description of an expl as a semiconductor suggests a new mechanism for initiation of primary and secondary expls, propIns and pyrotechnics, because a combination of a low-intensity static electric field coupled with radiation from ultraviolet light (Ref 13), from gamma and X-rays (Ref 127, p 2) or from electron beams (Ref 100) was found to result in initiation.

Incident radiation produces linear changes in electrical conductivity with dose (Ref 113) by the production of photocarriers. Initiation then
Table 12
Compositions of Pulsating Pyrotechnic Systems (from Ref 124)

<table>
<thead>
<tr>
<th>White Composition</th>
<th>Red Composition</th>
<th>Green Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Nitrate</td>
<td>Strontium Nitrate</td>
<td>Barium Nitrate</td>
</tr>
<tr>
<td>65%</td>
<td>65%</td>
<td>60%</td>
</tr>
<tr>
<td>Al/Mg Alloy</td>
<td>Al/Mg Alloy</td>
<td>Al/Mg Alloy</td>
</tr>
<tr>
<td>20%</td>
<td>18%</td>
<td>20%</td>
</tr>
<tr>
<td>Nitrocellulose</td>
<td>Dicyandiamide</td>
<td>Amm Perchlorate</td>
</tr>
<tr>
<td>7%</td>
<td>8%</td>
<td>7%</td>
</tr>
<tr>
<td>Amm Perchlorate</td>
<td>Amm Perchlorate</td>
<td>Potassium Perchlorate</td>
</tr>
<tr>
<td>5%</td>
<td>6%</td>
<td>5%</td>
</tr>
<tr>
<td>Sodium Oxalate</td>
<td>Potassium Perchlorate</td>
<td>Barium Perchlorate</td>
</tr>
<tr>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
</tbody>
</table>

Table 13
Pulsating Reactions (from Ref 98)

<table>
<thead>
<tr>
<th>Dependence of the Pulse Frequency on the Fuel Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% Pentaerythritoldinitrodiacrylate</td>
</tr>
<tr>
<td>50% Strontium Perchlorate-tetrahydrate</td>
</tr>
<tr>
<td>20% Fuel</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Pulse Frequency, cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methacrylate-methyl ester</td>
<td>1</td>
</tr>
<tr>
<td>Methacrylate-ethyl ester</td>
<td>300</td>
</tr>
<tr>
<td>Acrylic acid-methyl ester</td>
<td>700</td>
</tr>
<tr>
<td>Acrylic acid-ethyl ester</td>
<td>500</td>
</tr>
<tr>
<td>Methacrylate acid-isobutyl ester</td>
<td>0.5</td>
</tr>
<tr>
<td>Methacrylate acid-a-butyl ester</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dependence of the Pulse Frequency on the Perchlorate Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>A { Methacrylate-methyl ester 60%</td>
</tr>
<tr>
<td>Pentaerythritoldinitrate-diacrylate 40%</td>
</tr>
<tr>
<td>B Strontium Perchlorate-tetrahydrate</td>
</tr>
<tr>
<td>Ratio of A to B</td>
</tr>
<tr>
<td>70 30</td>
</tr>
<tr>
<td>60 40</td>
</tr>
<tr>
<td>50 50</td>
</tr>
<tr>
<td>40 60</td>
</tr>
<tr>
<td>30 70</td>
</tr>
</tbody>
</table>
occurs in response to an applied field. In the Russian literature this photoelectronic initiation is referred to as the "chemical avalanche effect" because of the dependence of the field intensity at initiation on the specimen thickness (Refs 50 & 61). Charge injection is known to cause a memory effect in Pb Azide (Ref 88).

Whereas currently most studies deal with azides, a similar effort devoted to other metal salts such as nitrates and chlorates would be an important step toward understanding electrical initiation of pyrotechnics, and conversely to making possible safe, non-expl igniters. For instance, a study by Maycock (Ref 4) shows that those azides, perchlorates, and nitrates in which the solid state shows absorption on the long wavelength side of the anionic excitation band in soin, are the most unstable members of the respective series. Consequently, there is a direct relationship between the absorption spectra of pyrotechnic oxidizers and their respective sensitivities.

A promising approach toward controlling the static and impact sensitivity of initiators has consisted of co-precipitating the primary expl on a carrier or doping it in a manner which affects its solid state characteristics (Ref 97).

Oscillatory Reactions

Occasionally new pyrotechnic phenomena are discovered (Refs 98, 99 & 124) which may see application in special situations. An example is the development of pulsating burning pyrotechnics which constitute the optical analogue to the familiar whistling compus (Ref 138, Formulas 156–60). Whereas pyrotechnic whistles have a frequency of 2000 to 5000 cps, the new compus burn in the range of 0.1 to 700 cps and are therefore well suited for acquisition by electro-optical devices.

Pulsating burning systems were described by Gol'binder in 1961 (Ref 6) but which proved to be unsatisfactory. Siderov and Kravchenko published descriptions of their green and red flash compus (Ref 28) which are said (Ref 99) to be bright. New pulsating burning compus are reported by Wasmann (Ref 124) for white, red and green compus (Table 12). Copper chromite catalysts were used to adjust the pulse frequencies. The trick in making these reactions oscillate is said to be the selection of the correct Al/Mg alloy particle size distribution. Variation of signal frequency is reported by the use of the esters of acrylic acid and methacrylic acids and nitrate alcohols, as shown in Table 13. The explanation of the pulsating phenomenon remains unsatisfactory, and further study should be rewarding.

A composition for producing flickering signals was recently patented (Ref 126) which employs ingredients similar to those listed in Table 13.

New Technology

New process technologies (Ref 53) such as jet mills (Fig 2) and co-precipitation (Ref 97) may allow safe compounding of sensitive or toxic formulations. New analytical tools such as neutron radiography (Ref 92) afford improved non-destructive testing of devices. X-ray fluorescence (Ref 93) and neutron activation (Ref 94) provide quantitative analysis of pyrotechnic compus and their trace contaminants.

9) The Literature of Pyrotechnics

Military pyrotechnics, in contrast to civilian pyrotechnics, is well documented, although much of the useful device-oriented literature is either outdated or classified. Pyrotechnics as a science sees only limited attention and much current work is reported only in proceedings of meetings because, with some exceptions, there are few recognized journals which are suited to the subject.

Periodically, useful generalized reviews and explanatory expositions are published such as the series of books by A.A. Shidlovsky (Ref 149), by H. Ellern (Ref 138) and by G.W. Weingart (Ref 140); of these, Ellern's book is the most current and filled with a wealth of background information.

Among the more specialized books is the recent "Handbook of Pyrotechnics" by K.O. Baurer (Ref 152) which covers, its title notwithstanding, chiefly aspects of ordnance engineering as it applies to space technology, unlike the "Aerospace Ordnance Handbook" (Ref 133) which contains useful information on pyrotechnics which is not restricted to space applications. For civilian pyrotechnics, the Rev. R. Lancaster's book (Ref 145) is current, while the history of pyrotechnics in antiquity was scholarly presented by J. Partington (Ref 130).

General encyclopedias are usually poor sources of information except for Ullmann's
(Ref 136) discussion of civilian pyrotechnics, of matches, and of explosives. Twenty years ago the Denver Research Institute prepared an exhaustive review of small arms incendiary munitions (Ref 129). In order to fill the gap in the missing basic data on specialized applications, the US Army has published an "Engineering Design Handbook Series" (Refs 131, 132, 134, 143, 146, 147, 150 & 158). Of a long list of Government issued manuals, one on "Small Arms Pyrotechnics" (Ref 33) and one entitled "Joint Munitions Effectiveness Manual, Weapons Characteristics" (Ref 159) are recommended for complete description of the design and performance of US Military pyrotechnic devices. Corresponding data on space shuttle hardware is available from NASA (Ref 157). The Bermite Corporation published a collection of igniter compns (Ref 139).

Fundamental research in pyrotechnics is published in the US in "Combustion and Flame" by the Combustion Institute, and in the UK in "Combustion Science and Technology" and in "Fuel". Germany has the new journal, "Propellants and Explosives" (German Chemical Society), which is the successor to the discontinued "Explosivstoffe". A necessary caveat is that these journals are strongly oriented toward combustion or propulsion so that only rarely do they yield pyrotechnic information. Likewise, the various publications of the learned societies contain much data on thermodynamics, spectroscopy, and instrumental analysis which are useful in the study of pyrotechnics. In the USSR the situation is somewhat better as "Physics of Combustion and Explosion" (Fizika Gorenia i Vzryva) of the Siberian Branch Academy of Sciences USSR is exclusively oriented toward subjects of interest, as several scientific institutes are primarily devoted to research in pyrotechnics. The same authors do publish also, however, in the journals of the Academy of Science USSR (of which there are several) as well as in the corresponding journals of the academies of the various republics, so that the impression is created of a high level of activity.

The principal means of information exchange in the US has been at meetings which have been sponsored biannually by the Franklin Research Institute (Refs 142, 154 & 161), and by the Denver Research Institute (Refs 137, 141, 144, 153 & 160). Patent literature is often a convenient reference source. Itemized references and general references follow. The appended numbers with the prefix AD signify that the document is available from Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314.

Written by A. P. HARDT


P 524


Pyrotolites. Cast or pressed mixts of Tetryl and TNT, first studied and proposed in Fr in 1907 by Koehler and Marqueyrol, but not used at that time. Following is a list of the mixts proposed by them:

<table>
<thead>
<tr>
<th>Tetryl</th>
<th>TNT</th>
<th>Fusion Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>80.7</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>68.0</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>59.5</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>65.5</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>67.5</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>68.0</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>67.0</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>73.5</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>72.5</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>106.0</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>128.5</td>
</tr>
</tbody>
</table>

These mixts were later used in the USA and other countries (See under Tetryl)

Ref: L. Desvergnes, MP 19, 265–66 (1922)

Pyroxalam. The name given by Uchaitius in the 1830's to a white powder obtained by nitrating starch with a mixt of nitric and sulfuric acids, and which contained about 11.1% N. It was Nitrostarch (see in this Vol) with the formula C_{24}H_{32}O_{12}(ONO_{2})_{8}, and closely resembled a product previously prepd (1832) by Bracconnot by treating starch with neat conc nitric acid

Ref: Daniel (1902), 459, under Nitramidolon

Pyroxyle. A generic term applied to various kinds of NC prepd by the nitration of either cotton, wood, paper, jute or ramie

Ref: Daniel (1902), 665

Pyroxylics. Fr sporting powders, invented in the 19th century by Bruneau, contg NC 83 and Amm bichromate 17%. "Poudre J" and "Poudre S" were known by this name

Ref: Daniel (1902), 385 & 665

Pyroxyline. A group of Nitrocelluloses with N content ranging from 10% and less to about 12.65%. The lower N members (see also under Collodion Cotton in Vol 3, C394-R) are used
for the prepn of celluloid, pharmaceutical products and lacquers. The higher N members find use in the prepn of Dynamites and smokeless powders (see under Pyrocollodion and Pyrocellulose in this Vol)

Pyroxylins may be divided as follows:

a) **Pyroxylin for Smokeless Powder.** This includes Pyrocollodion (about 12.44% N) and Pyrocellulose (12.6–12.7% N). It is nearly completely (about 99%) sol in eth-alc, acet, acetate esters, etc.; partly sol in methanol; b) **Collodion Cotton** (Soluble Pyroxylin or Varnish Cotton) – see under Collodion Cotton; c) **Celluloid Pyroxylines.** Contain about 10.7% to 11.25% N, partially overlapping the Collodion Cotton range. It is used chiefly in the manuf of celluloid, plastics and some lacquers. It is prepd to give higher viscosities than Collodion Cotton. Sol in eth-alc, acet, acetic esters, methanol, and many other organic solvents; d) Pyroxyllns contg 10.0–10.7% N are sol in some organic solvents, especially ethanol. They are not used in industry; e) Pyroxyllns contg less than 10% N are practically insol in organic solvents, and are not used in industry


**Pyroxyline.** An expl patented in Fr in 1887 by Antoine and Gruselle consisting of PA, Pb oxide and K dichromate. It was tested in 1888 by the CSE and found to be of no interest to the Fr Govt (Ref 1)

*Refs*: 1) L. Liouville, MP 2, 648 (1884–89) 2) Daniel (1902), 665

**Pyroxytol.** Synonym for Pyroxylin

**Pyruvic Acid (2-Oxopropanoic Acid, Acetylformic Acid, Pyrroracemic Acid, Brenztraubenäsure in Ger), CH₃COOHOH, mw 88.06, colorless lq, mp 11.8°, bp 165° decomps, d 1.267 g/cc at 15/4°. Miscible with w, alc & eth. Polymerizes and decomps on standing unless pure and kept in container with airtight closure. Can be prepd by distn of tartaric acid in the presence of K acid sulfate as a dehydrating agent. The distillate must be fractionated under reduced press


**Pyruvic Acid Nitrophenylhydrazones; Salts.** Ciusa and Musajo (Ref 2) prepd a number of mono-metallic salts of the o-, m- and p-nitrophenylhydrazones of the general formula (O₂N)C₆H₄.NH.N:C.CH₃.COOM, where M is a metal

Ragno (Ref 3) prepd a number of mono-metallic salts of 2,4-dinitrocomps of the general formula (O₂N)₂C₆H₃.NH.N:C.CH₃.COOM. They all proved to be more or less expl. The most expl was the Pb salt – it expld violently at about 240° when heated slowly in a capillary tube. Other salts did not expl when heated slowly, but simply decompd. They expld or deflagr., however, when heated rapidly in a capillary or test tube. Most of the salts were insensitive to shock


**Pyruvonitrolic Acid.** See under Acetimethyl-nitrolic Acid in Vol 1, A84-L