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CHARACTERISTICS OF NON-MILITARY EXPLOSIVES

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Research Triangle Institute

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FOREWORD

Information in this report was compiled in the performance of Contract DAAK02-73-C-0128 during the calendar year 1973 by the Research Triangle Institute for the Mine Detection Division, under the supervision of Dr. Karl Steinbach, of the U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia. Dr. Glenn E. Spangler was the Contract Technical Monitor and contributed substantially to the work in this report. The portion of the work contained in this report was sponsored by the U. S. Naval Explosive Ordnance Disposal Facility, Indian Head, Maryland, Research and Development Department, Mr. Edward A. Rice, Department Head. In addition to the individuals identified in the various sections, many others have participated in the performance of the work which is reported here. Their contributions are gratefully acknowledged. Dr. J. W. Harrison, of the Research Triangle Institute, was the Project Leader.

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CHARACTERISTICS OF NON-MILITARY EXPLOSIVES

1.0 INTRODUCTION

In the gathering of data on commercial explosives and explosive materials used for clandestine bomb fabrication, in principle, three sources of information exist: 1) the manufacturers of the various explosives, 2) the organizations that are known to employ violence and explosives to gain their ends, and 3) the open literature.

For up-to-date compositional information on presently manufactured explosives an attempt was made to obtain such information from all known U. S. manufacturers of explosives. The list of manufacturers contacted and the types of explosives they manufacture is given in Appendix A. This approach, however, proved to be futile on several grounds. Most of the manufacturers indicated that compositional data were proprietary and could not be revealed. It was also pointed out that "just because a composition is patented it does not mean that it is actually being used" and, finally, it was stated that "it is highly likely that there are many compositions that are used today and are not patented". Thus, except for two manufacturers, none indicated what the actual composition of the explosives they manufactured.

For some general information on the techniques and explosives used by organizations and individuals known to employ violence to gain their ends, the book by Stoffel on "Explosives and Homemade Bom's" [Ref. 1] is helpful. Certain parts of it have been summarized in the section "Homemade Bombs" of this report. Probably a more complete information could be obtained from major metropolitan police intelligence untits and the FBI. Thus, the major conclusions in this report are based on data obtained from the open literature. The various compendia examined for background information followed by a list of other serials and pertinent reviews on explosives research, permissible explosives, ammonium nitrate, slurries, evaluating hazardous chemicals, decomposition and combustion of perchlorates and compatibility of explosive: with polymeric materials are all given in Appendix B.

2.0 COMPOSITION OF THE EXPLOSIVES

In Appendix C are listed representative compositions of explosives of the various classes studied. Many of these represent compositions patented or described within the last few years. According to the literature, the major current activity is in the ammonium nitrate-fuel oil-additives class of explosives. Although we have listed the most examples of this class of explosives, proportionwise this still does not even begin to indicate the large amount of data available on these compositions.

2.1 Commercial Dynamites

Commercial dynamites comprise the following series of compositions: 1) straight dynamite (nitroglycerin the only high explosive in the composition), 2) straight gelatin dynamites (straight dynamite in whick nitroglycerin has been gelatinized most often with nitrocellulose; may also contain ethylene glycol dinitrate and other low molecular weight nitrocompounds); 3) extra dynamite (straight dynamite also containing ammonium nitrate); 4) extra gelatin dynamite (straight gelatin dynamite also containing ammonium nitrate); 5) permissible dynamite (any dynamite compositions in which the ammonium nitrate is the major constituent; such compositions may also contain a flame coolant); 6) blasting gelatin (a dynamite composition consisting of only nitroglycerin and nitrocellulose as the main components; the composition may contain as much as 10% of nitrocellulose).

Thus, the one characteristic volatile component present in practically all dynamite compositions is nitroglycerin. The rext two most characteristic volatile components are ethylene glycol dinitrate and paraffin wax, used

to impregnate containers containing the dynamites. Ethylene glycol dinitrate is the best freezing point depressant material and by far the most used in dynamites.

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According to Urbansky [Ref. 2] ("Explosives, Their Manufacture, Properties, Tests and History, Vol. 2, p. 149) in practice a 50/50 mixture of glycerin and glycol is usually nitrated to produce in one operation a product suitable for use in low-freezing dynamites. According to the work of Brandmer [Ref. 3] the vapor pressure of nitroglycerin and ethylene glycol dinitrate (EGDN) are as follows:

Nitroglycerin

Temperature , °C	30°	40°	50°
Vapor pressur ¹ , mmHg	0.0012	0.0030	0.0081

Ethylene Glycol Dinitrate

Temperature, °C	30°	40°	50°
Vapor pressure, mmHg	0.125	0.299	0.648

From the vapor pressure data on the pure components that Brandner had obtained he calculated the vapor pressures of various nitroglycerinethylene glycol dinitrate blends thus showing the contribution ethylene glycol dinitrate makes to the detectable vapors. These vapor pressures are shown in Table 1.

Table 1. Vapor Pressure of the Nitroglycerin-Ethylene Glycol Dinitrate Blends

T	'otal Vapor Pressu	re, malg	
30°C	40° C	50°C	
0.0186	0.0433	0.1002	
0.0345	0.1159	0.1841	
0.0624	0.1475	0.3314	
	30°C 0.0186 0.0345	30°C 40° C 0.0186 0.0433 0.0345 0.1159	0.0186 0.0433 0.1002 0.0345 0.1159 0.1841

However, such other nitroaromatics as mono- and dinitrotoluenes are alsc used for this purpose. Some of the other volatile components that have been used in dynamite compositions are: mono- and dinitrotoluene, TNT, formamide, ethylene glycol, tetralin, urea, kerosine, glycerol, fuel oil, diesel oil, light oil, spindle oil, turbine oil and motor oil. Fuel oil and the other oils all have components that have high vapor pressures and are easily detected. The various oils usually also contain a small amount of proprietary esters of phosphoric and sulfuric acids. The lower aliphatic glycols, formamide and urea are used to avoid plasticity loss in dynamites due to the presence of the various exidizers. Thus, it may be inferred that these substances should also be rather characteristic of dynamite compositions. All the available vapor pressure data on the above materials are recorded in Table 2.

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Nitrocellulose and nitroglycerin are two materials that are photolytically unstable. Thus, depending upon the composition (purity) and exposure conditions generation of nitrogen oxides takes place to various extents. The ratio of nitrogen monoxide to nitrogen dioxide generated from a source is thought to be rather characteristic of that source that is presumably constant [Ref. 4]. The implication being that by determination of such NO/NO₂ ratios, the source can be identified (inferred).

The most common container materials for dynamites and explosives in general are waxed paper, burlap and polyethylene. Of these three polyethylene is gaining in usage mainly because of its excellent moisture

Material	Vap. Press. at 25°C(torr)	Ref.
NG	5×10^{-3}	1,2
INT	3×10^{-6}	4
EGDN	0.07	3
o-Nitrotoluene	0.20	1,2
2,4-Dinitrotoluene	1.7×10^{-3}	4
Formamide	0.02	5,6
Ethylene glycol	0,12	5
Tetralin	0.40	1,2
Urea	1×10^{-5}	6
Glycerol	2×10^{-4}	5,6
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Table 2. Vapor Pressure Data on Selected Components of Dynamites

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- Coates, A. D., Freedman, E. and Kuhn, L., "Characteristics of Certain Military Explosives," Ballistic Research Lab., Report No. 1507, Aberdeen Proving Ground, Md., November, 1970, AD877635.
- 5. Riddick, J. A. and W. B. Bunger, Organic Solvents, Physical Properties and Methods of Purification, 3rd edition, Wiley-Interscience, N. Y., 1970.

6. Calculated from Clausius-Clapeyron eq'n: log $p = A - \frac{B}{T}$.

Handbook of Chemistry and Physics, 47th edition, The Chemical Rubber Co., Cleveland, Ohio, 1966.

^{2.} Extrapolation of log p vs 1/T plot.

Jordon, T. E., Vapor Pressure of Organic Compounds, Interscience, N.Y., 1950.

barrier properties. Its growth is tempered, however, by economic considerations. The inherent flexibility of polyethylene means that no low nolecular weight plasticizers are needed for it. To the best of our knowledge no permeability measurements of EGDN or NG or the blends of the two through polyethylene and paper exist. Such measurements are vital in the assessment of effective detection methods of the vapors.

2.2 PETN

A commercial use of PETN explosives is in the explosive forming of metals. Such formulations involve the use of polymeric binders of many different types, for example: silicon oil, polyurethanes, epoxy, polyether, polyacrylates, butadiene-acrylonitrile copolymers, etc. As a result, plasticizers (for example, dioctyl azelate), antioxidants (nonylphenyl phosphite) and catalysts (iron or lead naphthenates) mry also be present in such compositions. The only characteristic component of all PETN explosive compositions is PETN itself. Its vapor pressure at 20°C has been given as 1.1×10^{-8} torr (Ref. 4 in Table 2).

Although in many cases the polyurethane binder is prepared <u>in situ</u>, because of the great reactivity of the diisocyanates (toluen_ diisocyanate, hexamethylene diisocyanate) in general, little if any free monomer would be expected in such formulations.

2.3 AN/Fuel Oil Compositions

The importance of AN-Fuel Oil compositions as industrial explosives can not be overemphasized. In 1969 approximately 2.2 billion pounds of explosives were consumed and better than 84% of that amount were AN containing compositions. The composition of the explosives by

product groups consumed that year is best illustrated in Fig. 1, taken from a Bureau of Mines Circular [Ref. 5]. The term "unprocessed ammonium nitrate" refers to AN purchased in bulk form for onsite mixing with fuel oil. The black powder share of the market at that time was less than 0.02%. In Fig. 2 [Ref. 5] is illustrated the apparent consumption of industrial explosives by the type of industry. The position of coal mining as the major consumer is primarily due to the large amounts of AN-FO used in stripping. The railway and construction, quarrying and nonmetal mining, and metal mining industries each consume roughly 20% of the total. The trend for the various groups of explosives is as follows: slurry explosivesincreasing high explosives-constant, permissible explosives-decreasing, rigidly cartridged explosives-decreasing, liquid oxyger explosives-decreasing, black powder-decreasing, dry blasting agents and unprocessed AN-increasing.

The oxygen-balanced atamounium nitrate-fuel oil composition contains 94.5% AN and 5.5% FO. Because the CO produced from an overfueled composition is less toxic than NO and NO₂ from an underfueled composition, a slight oxygen deficiency is preferrable and thus the common ANFO mixture for field use is 94% AN and 6% FO. Although the simple ANFO mixture is optimum for highest energy release per unit cost of ingredients, often compositions with different energies and densities are desired. For this reason thousands of different formulations of ANFO compositions have been and are continually formulated.

The one most characteristic component of all ANFO compositions is a variable mixture of hydrocarbons known also as: fuel oil, diesel oil, light oil, spindle oil, turbine oil, motor oil, paraffin wax and kerosene. All of these materials consist of a mixture of linear and branched alkanes.





Fig. 2. Apparent consumption of industrial explosives in the United States in 1969 by industry.

as the major components and can be rather easily detected by their characteristic odors. Loss of an appreciable amount of the oil by evaporation or migration is a const....t problem with these compositions and the oil migration is easily apparent from the oil staining of the containers. Most ANFO compositions also contain low molecular weight nitro compounds such as: nitrobenzene and dinitrotoluene and in some compositions-trinitrotoluene. These materials, with the exception of TNT, are materials that have high vapor pressure and are easily detected. Such other materials as: benzene, styrene, ethylene glycol, diethylene glycol, formamide, urea, acetone and glycerin have also been used in ANFO compositions. As most of these same components, including the oils, are also used in certain dynamites, the identification of the two types of explosives by just their detectable vapors may not be always easy.

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A new family of products, known as "Tovex" water gel explosives were developed by DuPont to meet the modern day requirements of large volume iron ore mining techniques [Ref. 6]. Tovex is delivered in either polyethylene bags or through bulk pump trucks. Tovex consists of a cap insensitive chemical composition of non-nitroglycerin highexplosive ingredients. It is the first TNT sensitized water gel explosive marketed by DuPont. It has a density of 1.4, has good resistance to freezing and has excellent shelf life during hot weather storage. Several grades of Tovex are manufactured today. "Super Tovex" is a higher density version of "Tovex". "Tovex A-2, A-4 and A-6" provide a graded strength series of aluminum containing water gel explosives. A-6 has the highest density (1.6) and the highest theoretical strength. In research on water gel explosives it was noted that water gel explosives containing increased amounts of TNT

gave performance much superior to that which had been predicted by theoretical concepts and computer studies. Thus, a new series of "Tovexes 30, 35 and 40" are also now offered by DuPont.

Most of the available vapor pressure data on the more volatile components in ANFO compositions are assembled in Table 3.

Table 3. Vapor Pressure Data on Selected Components of ANFO Explosives

Material	Vap. Press. at 25°C(torr)	Ref.	
Fuel oil Diesel oil	~ 0.1 ~ 0.1	3	
Light oil Spindle oil	<u>95</u> ~ 10 ⁻⁴	3	
Turbine cil Mctor oil	- 10 ⁻⁴ - 10 ⁻⁴	3	
Paraffin wax	~ 10-4	3	
Kerosene Nitrobenzene	~ 4 0.28	3	
Dinitrotoluene Trinitrotoluene	$ \begin{array}{c} 1.7 \times 10^{-3} \\ 3 \times 10^{-6} \end{array} $	4	
Benzene	95	5	
Styrene Ethylene glycol Diethylene glycol	6.5 0.12 0.01	5 5 1,2	
Formaride Urea	0.02 ~ 10 ⁻⁵	5,6	
Glycerir	2×10^{-4}	5,6	

- Handbook of Chemistry and Physics 47th edition, The Chemical Rubber Co., Cleveland Ohio, 1966.
- 2. Extrapolation of log p vs 1/T plot.

- 3. R. E. Kirk, D. F. Othmer, "Encyclopedia of Chemical Technology, 2nd edition, New York, Interscience Pub., Inc., 1963.
- Coates, A. D., Freedman, E. and Kuhn L., "Characteristics of Certain Military Explosives," Ballistic Research Lab., Report No. 1507, Aberdeen Proving Ground, Md., November, 1970, AD877635.
- 5. Riddick, J. A. and W. B. Bunger, Organic Solvents, Physical Properties and Methods of Purification, 3rd edition, Wiley-Interscience, N. Y., 1970.

5. Calculated from Clausius-Clapeyron eq'n: log $p = A - \frac{B}{T}$.

The uncertainty about the exact composition of the various oils, especially as to the various proprietary additives that are used in such materials, makes this the least exact identification.

2.4 Black Powders

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The formula of black powder has changed little over the years consisting basically of 75% potassium or sodium nitrate (chile saltpeter), 15% charcoal, and 10% sulfur. Bituminous coal or activated carbon have also been substituted for charcoal and graphite is used to impart a glaze finish to the final product where free-flowing and non-lumping characteristics are desired.

Black blasting powder is a definitely grained material which is normally supplied as a glazed material. The glazed finish is obtained in the final stage of manufacture by tumbling the powder in contact with a small amount of powdered graphite. There are two types of black blasting powder - one containing potassium nitrate and the other sodium nitrate.

Black powder pressed into cylindrical pellets is known as "Pellet Powder". The composition of Pellet Powder is basically the same as that of black powder containing sodium nitrate and modified slightly by the addition of additives to control the physical and explosive properties [Ref. 6]. We have not been able to obtain information on such additives. Thus, we find no components of sufficient volatility in black powder compositions.

2.5 Smokeless Powders

Smokeless powder compositions may be subdivided broadly into two groups: 1) those consisting of nitrocellulose, nitroglycerin and diphenylamine compositions, and 2) those which contain other components in addition to the ones given in 1) with or without the nitroglycerin. Nitrocellulose is the main component

in all compositions and nitroglycerin content varying anywhere from 0 to 43.0%. The other characteristic component that all smokeless powder compositions contain is diphenylamine which is used as the stabilizer for NC. Most of the smokeless powder compositions also contain a detarrent (material that retards deflagration of the powder) which can be a low molecular weight material as, for example, dibutyl phthalate, or such high molecular weight materials as: graphite, polyurethane, poly(vinyl acetate), poly(vinyl butyral) acrylic esters, cellulose acetate or melamine-formaldehyde condensation polymer. When polymeric deterrents are used the following solvents have been employed: methanol, iso-butylmethyl ketone, ethanol, CH_2Ct_2 , and CCt_2FCF_2Ct . Supposedly, all of the solvents are removed from the final product once the deterrent coating application has been completed.

Practically all smokeless powder compositions just as the straight gelatin dynamite, extra gelatin dynamite and blasting gelatin contain NG-NC as the explosive components. The difference between the smokeless powder and dynamite compositions is that in the smokeless powder compositions NC is the major component while in the dynamites NG is the major component. As far as the commercial uses of smokeless powder are concerned they are limited, because smokeless powders are too expensive. What commercial usage there is (mainly for small arms propellants) depends primarily upon the availability of government suplus stocks [Ref. 5]. According to one smokeless powder manufacturer, a composition that contains no nitroglycerin is used commercially for oil well tools and other special applications.

Some of the available vapor pressure data on the more volatile components in smokeless powder compositions are listed in Table 4.

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Material	Vap. Press. at 25°C(torr)	Ref.
NG	5×10^{-3}	1,2
DPAm	5×10^{-2}	3
DBP	2×10^{-4}	3
isoButyl Methyl Ketone	5	3
Resorcinol	2 × 10 ⁻⁴	1,2
Triethylene glycol dinitrate	~ 10 ⁻⁴	4

Table 4. Vapor Pressure Data on Selected Components of Smokeless Powder Compositions

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 Handbook of Chemistry and Physics, 47th edition, The Chemical Rubber Co., Cleveland, Ohio, 1966.

2. Extrapolation of log p vs 1/T plot.

3. R. E. Kirk, D. F. Othmer, "Encyclopedia of Chemical Technology, 2nd edition, New York, Interscience Pub., Inc., 1963.

4. Calculated from Clausius-Clapeyron eq'n: log $p = A - \frac{B}{T}$.

2.6 Chlorates/Perchlorates-Combustibles Compositions

Chlorate explosives in general are more sensitive than the other types of explosives and, hence, no large scale commercial uses exist for them. Characteristically, the better known chlorate explosive compositions are of early origin and have been described in the "International Critical Tables" of 1930 and Marshall's book on "Explosives, Their History, Manufacture, Properties and Tests" of 1917. Two present day commercial uses of chlorates are in match head compositions and photoflash powders. A modern day use for chlorate explosives may develop for the inflation of safety air bags in automobiles. The perchlorates are also used in the above described applications and have the advantage over the chlorates in that they are more stable and less sensitive. Consequently, they have been used in several smaller scale commercial applications including mining.

The characteristic components of the chlorate explosives are sodium chlorat. and/or potassium chlorate. Of the perchlorates--potassium perchlorate is the characteristic component as ammonium perchlorate is much too sensitive for such applications. Some of the corbustible components are used: nitroglycerin, nitrocellulose, mono- and polynitrotoluene, benzene and naphthalene, nitrated resins, paraffin wax, fuel oil, castor oil and glycerin. The available vapor pressure data on some of the components of chlorates/perchlorates-combustibles are given in Table 5.

Table 5. Vapor Pressure Data on Selected Components of Chlorates/Perchlorates-Combustibles Compositions

Material	Vap. Press. at 25°C(torr)	?.ef.	
 NG	5×10^{-3}	1,2	
o-Nitrotoluene	0.20	1,2	
Nitrobenzene	0.28	3	
Paraffin wax	~ 10 ⁻⁴	4	
Fuel oil	~ 0.1	4	
Glycerin	2×10^{-4}	3,5	

- Handbook of Chemistry and Physics, 47th edition, The Chemical Rubber Co., Cleveland, Ohio, 1966.
- 2. Extrapolation of log p vs l/T plot.

- 3. Riddick, J. A. and W. B. Bunger, Organic Solvents, Physical Properties and Methods of Purification, 3rd edition, Wiley-Interscience, N. Y., 1970.
- 4. R. E. Kirk, D. F. Othmer, "Enclopedia of Chemical Technology," 2nd edition, New York, Interscience Pub., Inc., 1963.
- 5. Calculate: from Clausius-Clapeyron eq'n: log $p = A \frac{E}{T}$.

2.7 Photoflash Powders

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All the photoflash compositions that we have been able to find contain a chlorate or a perchiorate as the oxidant. The composition can be as simple as a mixture of two perchlorates (lithium and sodium) and aluminum powder, or as complex as one consisting of ten components. Invariably the compositions contain a metal powder in addition to the chlorate or perchlorate and no solvents or liquids are involved in the formulation of such compositions. In multicomponent formulations, melt mixing of eutectic mixtures of perchlorates with other components is involved during preparation. Such other materials as red phosphorus, sulfur trichlorophenol, magnesium oxide, hydroxyethylcellulose have been used. Components with appreciable vapor pressures are not used in appreciable amounts in photoflash powders.

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2.8 Match Heads Compositions

Discounting the early match compositions, the first safety matches were developed in 1855 which used red phosphorus on the side of the box [Ref. 7]. In 1898 the "strike-anywhere" match was developed which used phosphorus trisulfide in the match head. It has long been recognized that the adhesive in the match head composition is one of the most important components of the match if it is to function properly and that animal glue is the best adhesive for this purpose. Two adhesive mixes are used in match production: 1) the base mix, and 2) the tip mix. The former is applied directly to the stick and a pure hide glue is used for this purpose with just the "right" foaming characteristics. The glue used in the tip mix must be completely grease free and must possess high foaming characteristics in order to provide a light mixture. The purpose of the incorporation of air into the match head mix is to insure a slow, even burning. A match head

composition can be made into a powerful explosive by simply eliminating the air bubbles from the mix which is a direct function of the glue used in the composition.

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Match head compositions are complex consisting of as many as 11 components. Furthermore the density of the mix has to be just "right" for the material to burn slowly rather than explode. Various types of adhesives are continually being developed, however, animal glue has not been surpassed in this application. The characteristic and major component of match head compositions is an inorganic chlorate or a perchlorate. Animal glue is the second characteristic component in most compositions with all kinds of synthetics being a distant second choice. The third characteristic component is a filler which is comprised by one or several of the following: diatomaceous earth, ground glass, sand, kieselguhr, powdered asbestos, mica powder, and quartz powder. Apparently all compositions also contain a few percent of elemental sulfur. Such other materials as: shellac, TiO,, a pigment, starch, ZnO, resorcinol, wood resin, poly(vinyl alcohol), potassium dichromate and gelatin constitute some of the other components in the formulations. Thus, only small amounts of volatile components are found in match head formulations. The bulk (>50%) of the composition is comprised by the chlorates/perchlorates and various inert fillers. In some rare cases, a composition may contain more than 30% of animal glue or an organic sulfide as part of the composition. However, such compositions can not be regarded as characteristic of most match heads. Animal glue appears to be the only characteristic source of volatile components from match heads. The calculated sulfur vapor pressure at 25°C is 4×10^{-4} torr which may be sufficient for detection purposes.

2.9 Summary of Characteristic Components

The "volatile" components (characteristic and otherwise) in the various explosive compositions are commarized in Table 6. Commercial dynamites as well as smokeless powder contain NG and NC as the characteristic volatile components. In addition, present day dynamites also contain ethylene glycol dinitrate as a characteristic component. The characteristic volatile component of PETN explosives in PETN itself. The characteristic volatile component of AN-Fuel Oil explosives is a complex mixture of straight and branched chrin hydrocarbons commonly known as oils of various types. Black powder, chlorates-combustibles, photoflash powder, and match heads do not possess a characteristic volatil. component although all of them may contain a non-characteristic volatile component.

Table 6.	Summary	of	"Volatile"	Components
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Explosive	Characteristic Components	Other Components			
Commercial Dynamites straight dynamite straight gelatin dynamite extra dynamite extra gelatin dynamite permissible dynamite blasting gelatin (dynamite)	NG; EGD, paraffin wax NG; NC; EGD; paraffin wax NG; EGD, paraffin wax NG; NC; EGD; paraffin wax NG; EGD, NC NG; EGD, NC	Mono-and dinitro toluenes, TNT, form- amide, ethylene glycol, tetralin, urea, kero- sene, glycerol, fuel oil, diesel oil, light oil, spindle oil, turbine oil, metor oil.			
PETN	PETN	Dioctylazelate, no- nylphenyl phosphite, silicone oil.			
<u>AN-Fuel Oil</u>	Fuel oil, diesel oil, light spindle oil, turbine oil, paraffin wax, kerosene	Nitrobenzene, dinitro- toiuene, TNT, benzene styrene, ethylene glycol, diethylene glycol, formamide, urea, acetone, glycerin.			
Black Powder	None	Not Available			
Smokeless Powder	NC, NG, DPAm	DBP, isobutyl methyl ketone, resorcinol, triethylene glycol dinitrate,			

Table 6 cont.

Summary of "Volatile" Components		
Explosive	Characteristic Components	Other Components
Chlorates/perchlorates- combustibles	None	NG, NC, mono and polynitrotoluene, benzene, naphthalene, paraffin wax, fuel oil, castor oil, glycerin.
Photoflash Powders	None	Trichlorophenol, sulfur
<u>Match Heads</u>	Sulfur	Animal glue, resorcinol.

An overall summary of various characteristic components according to their function in the various explosives is given in the Appendix D. The components were arranged into the following groups: stabilizers, oxygen carrying compounds, anti-acid materials, gelatinizing agents, binders, energizers, flame coolants, surfactants, compatibility agents and softening point depressants for binders, plasticizers, some combustibles, water proofing agents, fuel sensitizers for NH₄NO₃, freezing point depressants, gas formers, aerating agents.

3.0 HOMEMADE BOMBS

3.1 The Statistics [Ref. 1]

During hearings that were conducted in 1970 by the Senare Investigating Subcommittee on Explorives, the Justice Department reported on the results of a survey on bombings covering the period of January 1, 1969, through April 15, 1970. A total of 4330 explosive and incendiary bombings had occurred. Bombings had resulted in 40 deaths, 384 injuries. Property damage was estimated at 22 million dollars. In addition, there were 1475 attempted bombings and 35,000 bomb threats throughout the country.

3.2 Potential Bombers [Ref. 1]

A potential bomber can be loosely identified through his activities and association in an organization that is known to employ violence and explosives to gain their ends. The Ku Klux Klan (KKK) and the Students for a Democratic Society (SDS) are examples of this type of organization. Apparently schools for bombers have been conducted by such groups. Students for a Democratic Society has distributed pamphlets in which instructions on firebombs, napalm bombs and time bombs have been given.

Armed Forces schools have taught the largest number of individuals the functioning and use of explosives. In many instances, this training has been put to use upon the return of servicemen to civilian life.

A number of recent explosions of "bomb factories" have provided additional data on potential bombers and their methods. In the 1970 exploston of Greenwich Village, N. Y., town house, members of the SDS Weatherman faction were involved. Bomb components retrieved consisted of

dynamite, blasting caps, doorbell wire, clock timing devices and plumbing pipe. In Chicago, after a bomb factory explosion, sticks of dynamite, explosive liquid, and literature on bomb making were recovered. In a New York bomb factory explosion a Black Panther was killed and the following chemicals were recovered: potassium nitrate, ammonium nitrate, sulfuric acid, gasoline, smokeless powder and lead pipes.

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The 1969 study on the characteristics of bombers concluded that a potential bomber could not be identified by any detailed characteristics, but the composite characteristics indicated a young white male of upper middle class or wealthy background.

3.3 Explosive Sources

Most of the explosive incidents that confront police agencies involve one of the following sources:

- 1. Homemade bombs
- 2. Commercial explosives
- 3. Fireworks
- 4. War souvenirs and military ammunition
- Transportation accidents involving explosives
- Military aircraft accidents

dynamite, blas pipe. In Chio explosive lique York bomb fact chemicals were acid, gasoline The 1969 potential bom but the compor-middle class of 3.3 Exp. Mos involve one of 1. 2. 3. 4. 5. 6. While how involving the propellants v occur. Explor distance of m and military are not restra country. The does present sites may beo While homemade bombs dominate the explosives incidents, explosions involving the other sources do occur. Shipments of explosives and propellants via railroad and truck are made continually and accidents occur. Explosives in an accident may be scattered and thrown to a distance of many hundred yards. The seriousness about war souvenirs and military ammunition in civilian communities is the fact that they are not restricted to the larger cities but can occur throughout the country. The proximity of a large military installation in an area does present a problem of a continuing source of explosives. Construction sites may become sources of explosives as a result of pilferage or

inadventant "leaving behind" after completion of a construction project. For example, construction sites can be a major source of nitroglycerin. Fireworks are another serious source of explosives. Coupled with this is the fact that literature on how to "manufacture explosive fireworks in your own home" is available. For example, formulae for pyrotechnics from sugar, smoke powder, black powder, ammonium picrate, a plastic explosive, rocket mixtures and nitroglycerin are detailed in such sources.

3.4 Trends in Homemade Bombs

Prior to about 1968, most bombs employed were simple in const.uction and consisted of one or more sticks of dynamite with a nonelectric blasting cap and a fuse or a fuse and black poweer in a container. Since that time the trend toward the construction of more complex time bombs and the use of other triggering devices, such as anti-disturbance mercury switches, has become apparent. Small transistor batteries have been increasingly used as power sources for electrically initiated homemade bombs. Devices that will explode if cut into improperly or if disturbed are becoming more common. Explosive fillers of more variety than in the past are being used. This is due to the increased knowledge about explosives and increased numbers of individuals mixing their own explosive combinations. For example, explosive bombs using ammonium nitrate in combination with dynamite were used first during 1970 and are expected to become more common in the future.

3.5 The More Common Homemade Bomb Explosives

3.5.1 Black Powder

Black powder is primarily used in fireworks, primer compositions, ignition charges for smokeless powder, core-type safety fuses, and mining. The ingredients for homemade black powder may be also obtained easily by anyone in a drug store.

3.5.2 Smokeless Powder

The easiest method for the average individual to obtain smokeless powder is to purchase shotgun shells at various retail outlets and extract the powder from the shells. Black and smokeless powders do not require blasting caps to set them off, a simple homemade fuse will do.

3.5.3 PETN (Pentaerythritol tetranitrate)

PETN is used as the explosive core in detonating cord, as the explosive in new flexible explosive sheets, and as a boosting explosive in blasting caps. The flexible explosive sheet (Deta sheet, DuPont) consists of an integral mixture of PETN and a binder and has both military and commercial applications. The commercial form contains 85% PETN and a blasting cap is required for detonation.

3.5.4 Nitroglycerin (NG)

While nitroglycerin may be easily prepared by anyone desiring to do so, the criminal individual most likely obtains it by placing dynamite in boiling water ("cooking") and skimming the NG off the top.

3.5.5 Dynamite

Dynamite is a widely used commercial explosive in the United States and has been the favored explosive in the past for the homemade bomb constructor.

3.5.6 Ammonium Nitrate/Fuel Oil (ANFO)

Ammonium nitrate alone is too insensitive to be used as an explosive. Ammonium nitrate-fuel oil mixtures, on the other hand, are widely used in commercial blasting operations. Ammonium nitrate in contact with moisture and copper will form a very sensitive nitrate which is as sensitive as lead azide. ANFO explosives are sold either with the fuel oil in the mixture, or dry for mixing on the site.

3.6 Commercial Blasting Accessories

Common commercial blasting supplies and accessories such as time fuses, detonating cords and blasting caps are also used in many homemade bombs. Time fuses (safety fuse) are used to transmit a flame to a nonelectric blasting cap which then sets off the explosive charge. Most homemade bombs do not require a blasting cap, the fuse itself will set off the bomb. Time fuses contain a core of black powder that is tightly wrapped with a waterproofing outer core of fabric or plastic material. Time fuses may be ordered through various firework outlets or they may be homemade. Some variations of homemade fuses are: a cord dipped in flue followed by black or smokeless powder; potassium permanganate, flour and sulfur mixed together and inserted into a soda straw; potassium chlorate and sugar mixtures used in the same manner.

Detonating cord (explosive cord, Prima Cord) consists of a highexplosive cord of PETN contained in a waterproof wrapping. Detonating cord is used to transmit a detonating wave from an electric or nonelectric blasting cap through the length of the cord to directly explode an explosive charge. Detonating cord has the very high detonating velocity of 21,000 ft/sec. and does not require a blasting cap on the explosive charge end.

Blasting caps are of two types: electric and nonelectric. They are copper or aluminum tubes, closed at one end and filled with several highly sensitive explosives that form part of the overall explosive train.

Both electric and nonelectric caps contain an ignition charge of a sensitive explosive mixture, an intermediate charge that is generally lead azide explosive, and a base charge of tetryl (trinitrophenylmethylnitramine), PETN or RDX (cyclotrimethylenetrinitramine) explosive.

3.7 Modern Explosives

Two more recent developments in explosives technology are the "Jet-Axe" and "Astrolite Explosives". The Jet-Axe was specifically designed for fire department use. By the use of a linear-shaped charge the Jet-Axe provides the firefighter with a fast, safe method of forcible entry. The explosive used in the Jet-Axe is RDX and depending upon the model may contain from 2 to 6 ounces of RDX.

Astrolite Explosives are basically liquids that can be pumped into tubes, sprayed, poured into containers, soaked into the ground, squirted into cracks, and mixed at the site from two nondetonable components in containers. Modifying agents can turn the explosive into gels or rubberlike solios, sensitize the explosive or change a wide number of physical, chemical and detonating properties. Astrolite explosives were developed by the Explosives Corporation of America, and are based primarily on hydrazine nitrate.

4.0 DETECTABILITY OF EXPLOSIVE MATERIALS

In order to detect and identify explosive materials by trace gas techniques, several factors must be favorable. First, there must be volatile constituents in the explosive mixture. Second, there must be a mechanism of the transport of a sufficient amount of detectable volatile material from the vicinity of explosive mixture to the detector. Third, the detector must have sufficient sensitivity and a fast enough response time to indicate a response. Fourth, the response should be relatively unambiguous, i.e., the detector should be seleciive.

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The survey of sections 2.0 and 3.0 has indicated that several classes of explosive mixtures have volatile constituents that may be available for detection purposes. These are: commercial dynamites, ammonium nitratefuel oil (ANFO) mixtures, smokeless powder and -- perhaps -- homemade match-head bombs. The nature of the volatile constituents and possible means of detection are discussed below. Prior to that discussion, however, some perspective must be obtained on the availability of vapors for detection. A large variety of scenarios are possible. Exhaustive coverage of these is impossible because of the required detail and the fact that many specific parameter values are not available to give a good quantitative estimate of detection limits. However, it is possible to outline the factors which influence the transport of vapors from the vicinity of the explosive mixture to a region where they may be available for detection. This is done in Section 4.1. Section 4.2 considers the detection of commercial dynamite mixtures. Section 4.3 considers the detection of ANFO mixtures. Section 4.4 considers the detection of smokeless powder mixtures and methods of detection for homemade match-head bombs are discussed in Section 4.5.

In these discussions, it is assumed that no change is induced in the explosive mixture to improve detection, such as "tagging" with an easily detectable substance, or physically changing the explosive. As an illustration of the latter alternative, the use of nuclear radiation to improve detectability is discussed in Section 4.6.

4.1 Availability of Detectable Vapors

The detection of explosive mixtures by identifying characteristic vapors depends upon the availability of the vapors for the detection means. Consider the situation depicted schematically in Figure 3. An explosive mixture, 1, is enclosed in a container (primary barrier), 2. In the vapor space, 3, between the explosive and the container walls, there is a partial pressure of characteristic vapor, h_o . The composition of this vapor depends upon the concentrations of volatile constituents in the explosive mixture.

Due to permeation through the container walls or perforations, there may be leakage resulting in a mass flowrate, ϕ , of characteristic vapors from the primary barrier into the surrounding vapor space, 4. If ϕ_1 does not exceed the vaporization rate of volatiles from the surface of the explosive mixture, the partial pressure, h_0 , will be the equilibrium partial pressure, which is the maximum attainable.

The mass flowrate ϕ , will establish a partial pressure, h_1 , of vapor in the non-equilibrium vapor space, 4, beyond the primary barrier. The manner in which h_1 varies as a function of distance from the primary barrier will depend upon how this vapor space is bounded. If there is a secondary barrier (e.g. a suitcase in which several dynamite sticks are contained), and the mass flowrate, ϕ_2 , through this secondary barrier is small compared to



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1 Explosive Mixture

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- 2 Vapor space with vapor in equilibrium with solid
- 3 Primary barrier (container walls)
- 4 Non-equilibrium vapor space
- 5 Secondary barrier
 - Figure 3. Schematic Representation of Detection Methods

the primary mass flow rate, ϕ_1 , the partial pressure h_1 may approach uniformity. If there is no secondary barrier, the spatial variation of h_1 will be determined by eddy-diffusion of the characteristic vapors.

If the secondary barrier, 5, does exist the mass flowrate ϕ_2 and eddy-diffusion will determine the spatial variation of partial pressure h_2 around the barrier. As with the primary barrier the mass flow may be due to either permeation through the container walls or capillary flow through cracks or perforations. For either case the flow rate depends upon the difference between concentrations on either side of the barrier.

In the case of permeation of the ith species in the vapor phase, the mass flowrate per unit area of surface of the k^{th} barrier is [Ref. 8]

$$\frac{1}{A_k}\phi_k = \frac{M^i P_k^i}{22,400 t_k} (h_{k-1}^i - h_k^i)$$
(4.1)

where

 $A_k \equiv \text{surface area of the } k^{\text{th}} \text{ barrier, } \text{cm}^2$ $t_k \equiv \text{thickness of the } k^{\text{th}} \text{ barrier, } \text{cm}$ $P_k^i \equiv \text{permeability of } i^{\text{th}} \text{ species in } k^{\text{th}} \text{ material}$ $M^i \equiv \text{molar mass of } i^{\text{th}} \text{ species, } g$ $h_{k-1}^i, h_k^i \equiv \text{partial pressures of the } i^{\text{th}} \text{ species on either}$ side of the barrier, cmHg.

The coefficient P_k^i depends upon the diffusion coefficient, D_k^i , and the solubility factor, S_k^i , of the ith species in the kth barrier material. With the units used above, p_k^i has units of cm³ of gas at STP-cm/cm²-sec-cmHg. For permeation to occur, the characteristic vapor must be soluble to some extent in the barrier material, and capable of diffusing through the barrier from the high concentration side to the low concentration side at a reasonable rate.

If there are cracks, pores or perforations in the barrier, the mass flow of explosive vapor will be determined by vapor phase diffusion characterized by a diffusion constant D. This "constant" can be derived from gas kinetic theory in the form

$$D = \frac{1}{2} \lambda \overline{\upsilon} \phi \tag{4.2}$$

where λ is the mean free path in air for the diffusing molecule, \overline{v} the average thermal velocity for the diffusing molecule and ϕ a numerical factor which depends upon the nature of the collisional processes between the diffusing molecules and those of air [Ref. 9]. Using the standard expressions for λ and \overline{v} derived from gas kinetic theory, it can be shown that to a first approximation D is proportional to the three-halves power of temperature, T. For an aperture of cross-sectional area A, and length λ the mass flow rate will be given approximately, by

$$\phi = 1.6 \times 10^{-4} \frac{M^{1}AD}{T\ell} \left(h_{k-1}^{i} - h_{k}^{i} \right).$$
(4.3)

From the data given by Jost for some organic compounds in air, page 412 in Reference 9, a typical value for D is about 8×10^{-2} cm²/sec at 30°C and 1 atmosphere.

In order to gain some perspective on the relative mass transport rates we will use the following model situation. It is known that at 25°C the permeability of 2,4,6-TNT in dimethyl silicone is about 2×10^{-5} cm²(STD) cm/cm²-sec-cm Hg [Ref. 10]. Consider a block of TNT wrapped in dimethyl silicone of thickness 0.1 cm with a surface area of 160 cm². Assume that the vapor pressure inside, h_o, is the equilibrium vapor pressure of TNT at
25°C, about 10^{-7} cmHg [Ref. 11] and that the outside vapor pressure, h₁, is negligibly small compared to h₀. Using equation (4.1) the mass flow rate due to permeation is 2 x $10^{-1.3}$ g/c. Assume a single perforation of area 0.1 cm² in the film. The mass flow rate due to diffusion, from equation (4.3) will be about 10^{-12} g/s or about 5 times as large as that due to permeation.

In the case where pores, or perforations, are not straight, smooth walled tubes, there will be a reduction in the mass flow rate given by (4.3). This is a "tortuosity factor" which takes into account extra collisions due to the kinks along the path. Even with this reduction, however, the presence of several or many perforations greatly enhances the vapor transport and, therefore, the probability of acquiring a detectable amount of material.

4.2 Detectability of Commercial Dynamites

All commercial dynamites are based on nitroglycerin (NG), which is present in varying extent from about 10% up to about 75% by weight. The equilibrium vapor pressure of pure NG at 25°C is about 5×10^{-3} torr. Therefore, the equilibrium vapor pressure of NG above the various mixtures would be on the order of 10^{-3} torr. In addition, nitrated ethylene glycols may be used in varying percentages. Ethylene glycol dinitrate (EGD) has a vapor pressure about one order of magnitude higher than NG at 25°C. Depending upon the percentage used, the equilibrium vapor pressure above the explosive mixture may range from about 10^{-3} torr to 10^{-2} torr.

Both NG and EGDN are electron capturing compounds. Their detectability by instrumental methods such as the electron capture detector, negative

ion mass spectrometer or drift tube mobility spectrometer should be equivalent to 2,4,6-TNT and 2,4-DNT. The specifics of these detection methods and their capabilities are given in Reference 12. Depending upon the method used, the amount of material required for detection ranges from about 1 picogram up to about 1 nanogram.

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Since both NG and EGDN are condensible vapors at room temperature, there will be a strong tendency for these materials to adsorb to surfaces. For the model situation depicted in Figure 1, after a sufficient time period the outside of the primary barrier material and inside surface of the secondary barrier could be expected to have a moderate to high degree of coverage. This ease of adsorption can seriously deplete the amount of vapor available, but it also provides a possibility of concentration of enough material to enable detection if the adsorbed material is released from the surface. This is most conveniently done by heating. Heat could be applied to the whole container, or, if the container can be opened, like a suitcase, or the trunk of an automobile, the heat can be applied locally. This might be implemented with a resistance heated hotair gun or with an infra-red lamp. For coverage approaching a monolayer, the amount of material available per square centimeter will be on the order Therefore, heating of a few square centimeters would provide of a nanogram. plenty of material for detection.

Several methods have been developed for detection of dynamite by trace gas methods. One approach has been to use a noble metal such as gold or platinum to adsorb condensible vapor from a sample air stream. This is followed by desorptive heating in an inert gas stream to deliver the adsorbed

vapors to a gas chromatographic column for analysis. Detection of the elements from the column is accomplished with an electron capture detector. This method, first developed by Dravnieks [Ref. 13], who used a gold foil adsorption surface, has been modified to make a semi-portable commercial detection instrument which utilizes a platinum wire spiral as an adsorption surface [Ref. 14]. Further design improvements have been made to develop another commercial portable detection instrument [Ref. 15]. Only one of these instruments, the Hydronautics-Israel VTA, has been evaluated [Ref. 12, 16]. The detection limit for TNT, about 1 nanogram, should be about the same for NG and EGDN.

Another approach has been to use a dimethyl silicone membrane to separate condensible explosive vapors from atmospheric gases and to detect the presence of electron capturing species with an electron capture detec-The details of the principles involved in membrane separation have tor. been discussed by Spangler [Ref. 10]. One drawback is that the membrane is not as specific as a gas chromatographic column in the separation process. A commercial detector using this principle [Ref. 17] has been successfully used by the British Army in Northern Ireland. This instrument is subject to interferences by electron capturing species such as nitrobenzene (used in some shoe polishes), etc. In order to circumvent this problem, a dual channel method has been developed [Ref. 18] which uses a pyrolyzer in one channel to eliminate explosive vapor materials (which pyrolyze at a relatively low temperature) prior to impingement of the gas stream on a membrane separator. The differe: ~e in signal between the electron capture detectors in the pyrolyzed and : -pyrolyzed gas streams is proportional to the amount of explosive

material present.

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A commercial instrument using a membrane separation technique with a quadrupole mass filter for specificity and an electron multiplier for detection has been developed for explosives detection [Ref. 19]. Its size prohibits portability.

In addition to the electron capturing condensible vapors NG and EGDN, there is a probability that nitrogen dioxide (NO_2) may be found around dynamites which contain NG and nitrocellulose. Nitrocellulose spontaneously decomposes to release NO_2 [Ref. 20]. Since NO_2 is a common pollutant in ambient air, field measurement methods have been developed. One of the most commonly used depends upon the chemiluminescent reaction of NO (developed by catalytic conversion of NO_2) and ozone [Ref. 21]. The present detection limit for a commercial instrument of this type is about 1 ppb. Because of the variable concentration of NO and NO_2 in ambient air, there is a variable background level. A differential method of measurement which automatically subtracts background has been proposed by one manufacturer [Ref. 22]. The amount of NO_2 available from decomposing nitrocellulose will depend upon the decomposition rate and the flow through the barriers, discussed in Section 4.1.

4.3 Detectability of ANFO Mixtures

Ammonium nitrate based explosive mixtures contain varying amounts of hydrocarbons as the volatile constituents. Older recipes [Ref. 2.3] using nitrobenze or dinitrotoluene at about 4 to 6.5 weight percent provide electron capturing compounds which may be detected by an electron capture detector, as discussed previously in Section 4.2. The fuel oils used contain a veriety of aliphatic hydrocarbons with a wide distribution of mole-

cular weights. Appendix D, page D-7, gives some idea of the range of comnonents and their equilibrium vapor pressures. The heavier hydrocarbons such as paraffin wax and lubricating oil have very low vapor pressure. Fuel oil and diesel oils contain many lighter molecular weight fractions that have appreciable volatility at room temperature. It is these components that offer the best possibility for detection.

Several methods are available for measuring hydrocarbons. One of the most sensitive methods is the flame ionization detector (FID) which gives . response roughly proportional to the number of organically bound carbon atoms in the molecule. A commercial instrument is available [Ref. 24] which gives a precision of 0.05 ppm using an FID with a chromatographic column. This instrument has been used in the field, transported in a van, but is not portable. Infrared absorption measurement using a folded, multipath cell can be used to detect many hydrocarbons down to 0.1 to 0.5 ppm. A portable unit with a wavelength variable source and a path length adjustable from 3/4 meter to 20 meters is available commercially [Ref. 25]. Nondispersive IR with a multipath cell can also be used for measurement. Use of a wavelength at about 3.4 microns, which is the carbon-hydrocarbon bond stetch length, gives reasonable sensitivity. By pulsing IR radiation at an audio frequency and using an acoustically resonant detection cell, excellent sensitivity has been obtained for many atmospheric pollutant gases [Ref. 26]. However in the 3.4 micron region of interest for C-H bond detection, water vapor is an interferent [Ref. 27].

Because hydrocarbons · e extensively used legitimately, there will be many possible interferences which could render the use of hydrocarbon

detectors ineffective unless there are appreciable vapor leaks from the explosive mixture.

4.4 Detectability of Smokeless Powder Mixtures

Smokeless powders contain appreciable quantities of nitroglycerin and nitrocellulose. Nitroglycerin, is detectable with an electron capture detector, as discussed above in Section 4.2. Although nitrocellulose decomposes to release NO and NO_2 , diphenylamine is used to suppress the release and inhibit the decomposition. Until this suppressent is exhausted-determined by the shelf-life of the mixture as designed by the manufacturer-there will probably not be enough NO and NO_2 released for detection. However, if old, surplus smokeless powder is used to fabricate a bomb it is possible that the suppressent is at or near exhaustion and that enough NO or NO_2 can be given off to enable detection by a chemiluminescent detection technique.

4.5 Detectability of Match-Head Mixtures

The only "volatile" component of match-head mixtures is sulfur. This is present at about 4 to 8 weight percent. The most sensitive and specific detector for sulfur is the flame photometric detector (FPD), which uses a hydrogen-air flame and monitors characteristic sulfur emission at 394 nm. A sensitivity for elemental sulfur of 40 picograms has been reported [Ref. 28] since at 25°C the equilibrium vapor pressure of sulfur is about 4 x 10⁻⁴ torr, reduction to about 5%, based on composition, would give about 67 picograms per cm³. Allowing a reduction of 10⁻² for barrier effects, about 100 cm³ of air would have to be sampled to get a detectable signal. This might have to be concentrated to present the material as a detectable pulse.

4.6 Gas Enrichment by Means of Nuclear Irradiation

The data reported in this section are based primarily on the report of Rosenwasser [Ref. 29]. Both inorganic and organic explosives are considered. Lead azide [Pb(N₃)₂] evolved 4.5 to 5.6 ml of gas (S.T.P.) per gram after 47 x 10⁶ rads. After exposure practically pure nitrogen continued to evolve but at a reduced rate. Irradiation was also conducted at three different temperatures: -40°F, 72°F (ambient), and 160°F. After an exposure of 26 x 10⁶ rads, the gas formation at ambient temperature was 1.35 times that at -40°F and at 160°F 3 times that at -40°F. These values were adjusted for gassing at 160°F in the absence of radiation. Lead azide as well as some other explosives when irradiated at 160°F and then maintained at this temperature evolved more gas than could have resulted from the thermal effects alone.

Mercury fulminate $[Hg(CN=C)_2]$ upon irradiation evolves gas at a rapid rate (2.97 ml/g after 26 x 10⁶ rads) which increases with the time of exposure. Furthermore, gases continue forming after irradiation. Chemical analysis showed the offgas to consist of 71 vol. % CO₂ and 19% N₂.

Lead styphnate-



produced the smallest volume of gases of all of the explosives tested: 0.12 ml/g during exposure to 76 x 10^6 rads.

Diazodinitrophenol (DDNP)-



when irradiated at ambient temperature produced gas quantities similar to those from lead azide. Increasing amounts of gas were given off for incremental dosages. After 40 x 10^6 rads, a total of 7.2 ml/g was produced.

TNT is comparatively stable to gamma radiation. After 54×10^6 rads, gas evolution was only 0.14 ml/g. At $72^{\circ}F$ gas formation was 1.75 times that at $-40^{\circ}F$ and at $160^{\circ}F$ it was 7.5 times that at $-40^{\circ}F$.

Tetryl-



after 76 x 10^6 rads at 70°F produced 1.4 ml of gas per gram of tetryl. During the irradiation sufficient soluble impurity was formed to lower the melting point by 2°F. After 26 x 10^6 rads at 160° F tetryl evolved 4 times as much gas than at 72°F.

RDX-



after 40 x 10^6 rads evolved 1.8 ml/g. Additional gas continued evolving after irradiation was discontinued. The gas evolved appeared to consist of N₂, CO₂, and a trace of H₂. The evolution of gas tended to increase with increasing irradiation.

PETN-

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$$C(CH_2ONO_2)_4$$

during 38 x 10^6 rads irradiation at 72°F, 2.7 ml/g was evolved. This is much lower than that for nitroglycerin. However, the gas-evolution curve for PETN turns sharply upward after about 10^7 rads. The melting point of the irradiated material was depressed by 7°F.

In the case of binary explosives the volume of gas formed corresponded rather closely to the gassing characteristics of the major gas-producing component. Thus, for example-

Material, wt. %	Gas evolved during 26 x 10 ⁶ rais, ml/g (S.T.P.)
Tetrytol (65% tetryl, 35% TNT)	0.32
Baratol (67% Ba(NO3)2, 33% TNT)	0.09
Composition B (60% RDX, 40% TNT)	0.83
Tritonal (20% A1, 80% TNT)	0.09
Pentolite (50% PETN, 50% TNT)	0.24

Pure nitroglycerin decomposes under gamma irradiation rather easily producing 11.5 ml/g during 50 x 10^6 rads at 72°F. The decomposition gases corroded mercury which was not observed with the other explosives tested. The irradiated residue was very viscous and continued evolving fumes of NO₂.

Dried uncolloided nitrocellulose [Ref. 30] after irradiation to about 10^7 rads lost 1% of its nitrogen content. The intrinsic viscosity of the irradiated material was reduced to one third of its initial value.

The M-15 propellant consists of 54.7 wt. % nitroguanidine, 26% nitrocellulose, 19% nitroglycerin, 6% ethyl centralite (summetrical diethyl-

diphenylurea) and 0.3% cryolite (Na_3AlF_6) . A granular sample produced 3.35 ml of gas during 54 x 10⁶ rads exposure. Nitroglycerin would be expected to be the major source of the gas.

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Thus, the above data indicate that nitroglycerin is the most susceptible component to gamma radiation followed by lead azide, mercury fulminate, DDNP and PETN. For most cases reported, neither a qualitative nor a quantitative composition of data was available. Nitroglycerin was indicated to evolve considerable quantities of NO_2 .

5.0 SUMMARY AND RECOMMENDATIONS

A survey of commonly available explosive materials has indicated that mixtures based on dynamite are the most readily detectable by vapor phase detection methods presently available commercial instruments. There is a possibility that ANFO-fuel oil mixtures may be detected through hydrocarbon vapors and smokeless powders through NO₂ evolved in decomposition. A more remote possibility is the detection of sulfur vapor from match-head compositions.

As pointed out in Section 4 detection of vapors depends upon their availability, which is determined by the physical barriers to transport these vapors from the vicinity of the surface of the explosive mixture to the vicinity of the detector. If a serious effort is to be made to develop trace gas detection methods for hidden explosives we recommend that a part of this effort be a study of the characteristics of "barriers" commonly encountered, e.g. soils of different type, papers of different types and weights, cardboard, fabric, plastic films, etc. with respect to their ability to permeate the characteristic vapors from explosives.

Also of interest is the adsorption behavior of these vapors on various materials. The release of adsorbed vapors by the application of local heating represents a convenient method of obtaining a preconcentrated sample. In addition, it is possible that a needle probe of a suitable metal could be developed for insertion through a paper, plastic or leather coating to adsorb vapor which could then be released by inserting the needle into a detection instrument and heating. Therefore, we recommend that a study of the adsorption behavior of vapors from explosive materials be made to determine those circumstances favoring adsorption and release of vapor for detection by localized heating, e.g. by a laser beam.

Finally, the work cited on the use of nuclear radiation to degrade explosives has shown that gas may be evolved after gamma irradiation. However, only one compound, nitroglycerin, evolves a readily detectable gas, NO_2 . Since nitroglycerin based dynamites are detectable without such irradiation it does not appear productive to use this approach unless it can be established that low vapor pressure explosives like PETN and RDX also evolve NO_2 .

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APPENDIX A

Manufacturers of Explosives

1,3,4 AFACHE POWDER COMPANY Box 700 Benson, Arizona 85602

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- 1,3,4 AUSTIN POWDER COMPANY 3735 Green Road Cleveland, Ohio 44112
- 3,4 THE DOW CHEMICAL COMPANY 2020 Abbott Road Center Midland, Michigan 48640
- 1,2,3,4,5 E. I. DU PONT DE NEMOURS & CO., INC. Nemours Building Wilmington, Delaware 19898
- 1,2,3,4 HERCULES INCORPORATED 910 Market Street Wilmington, Delaware 19899
- 1,2,3,4 ATLAS POWDER COMPANY P. O. Box 2354 Wilmington, Delaware 19899
- 3,4 IRZCO CHEMICALS Suite 726, Kennecott Bldg. Salt Lake City, Utah 84111
- 3,4 MONSANTO COMPANY 800 N. Lindbergh Blvd. St. Louis, Missouri 63166
- 3 SIERRA CHEMICAL COMPANY 1490 E. Second Street Reno, Nevada 89502
- 1,3,4 TROJAN-U.S. POWDER DIVISION Commercial Solvents Corporation Allentown, Pennsylvania 18105
- 6 GEARHART-OWEN INDUSTRIES, INC. 1100 Everman Road Fort Worth, Texas 76101

APPENDIX B

100.00 52/CR4 5.52

Literature on Explosives

Compandia on Explosives

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 E. I. duPont de Nemours and Company, Inc. Wilmington, Delaware 19898.
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- "Active List of Permissible Explosives and Blasting Devices Approved Before December 31, 1972," Bureau of Mines Information Circular, No. 8597 (1973).

2 DIIN CORPORATION East Alton, Illinois 62024
- Pynamite
- Sokeless powder
- AIW
- Slurry Explosives
- PIN
- Black Powder

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9. C. Reeder, Chemical Engineering Progress, <u>64</u>, 49 (1968). A review on ammonium nitrate trends.

10. M. A. Cook, Industrial Engineering Chemistry, <u>60</u>, 44 (1968). A review on the development of slurries.

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- 11. R. D. Coffee, J. Paint Technology, <u>40</u>, 34A (1968). On evaluating hazardous chemicals.
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10. M. A. Cook, Industrial Engineering Chemistry, <u>60</u>, 44 (1968). A review on the development of slurries.

- 11. R. D. Coffee, J. Paint Technology, <u>40</u>, 34A (1968). On evaluating hazardous chemicals.
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Straight Gelatin Dynamites

NG	47.0%
DNT	3.0%
NC	1.3%
NaCO3	36.1%
Cereal	9.0%
Starch	2.7%
Chalk	0.9%

N. G. Johnson, C. A. Woodbury, U. S. 1,963,622, June 19, 1934

NG - Nitroglycol, 62-38%	39.2%
NC	2.5%
Ca(NO ₃) ₂	30.0%
Starch	11.7%
Pentolite [*]	12.5%
Fe203	4.1%
*petn/tnt	

R. Yokogawa, S. Mitsui, S. Asaka, M. Ata, Japan 71 20,159 June 5, 1971

Extra Dynamites

 $\begin{array}{ccccccc} NG & 12 & - & 25\% \\ NaNO_3 & 14 & - & 60\% \\ NH_4NO_3 & 7 & - & 50\% \\ Combustibles & 8 & - & 20\% \\ CaCO_3 & & 1\% \end{array}$

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"International Critical Tables," Vol. 7, First Ed., McGraw-Hill, N. Y., 1930, p.439

12.5%
1.0%
73.8%
5.0%
7.0%
0.7%

R. W. Cairns, U.S. 2,355,269, August 8, 1944

Extra Gelatin Dynamites

NG	60.0%
DNT	3.5%
NC	2.3%
NH4 ^{NO} 3	24.0%
NaNO ₃	2.2%
Cereal	6.0%
Starch	1.0%
Chalk	1.0%

N. G. Johnson, C. A. Woodbury, U. S. 1,963,622, June 19, 1934

NG	30.00%
DNT	2.00%
NC	1.13%
NH4NO3	57.78%
Sawdust	3.69%

Polyethylene glycol monostearate 0.40%

Pb0 2.50%

H. Sakai, K. Tsutsui, Japan 71 01,600, Jan. 14, 1971

NG - Nitroglycol	22.0%
NC	0.6%
NH 4NO 3	72.9%

Societe Francaise des Explosifs, Fr. 2,082,276, Jan. 14, 1972

NG - Nitroglycol, 1:4	32.8%
DNT	2.1%
NC	0.8%
NH4NO3	38.8%
NaNO3	19.1%
Wood pulp	3.5%
s ^o	1.6%
Chalk	1.0%
Expanded polystyrene beads	1.0%

F. E. Slawinski, U. S. 3,671,342, June 20, 1972



	0.4476
NH4 NO3	51.4%
NaNO ₃	18.4%
Hydroxypropylguar	0.5%
Chalk	0.3%

E. L. Falconer, U. S. 3,723,208, March 27, 1973

Permissible Dynamites

NG	29 %
AN	70%
Collodion cotton	1%

Melvin A. Cook, "The Science of High Explosives," Reinhold Book Corp., N.Y. 1968, p. 10

NG	30.0%
DNT'	2.0%
NC	0.7%
NaNO3	44%
NH 4 CL	15%
Starch	4.5%
Cereal	2.0%
Chalk	1.0%

N. G. Johnson, C. A. Woodbury, U. S. 1,963,622, June 19, 1934

Blasting Gelatins (Dynamites)

NG 92 - 93% NC 7 - 8%

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Melvin A. Cook, "The Science of High Explosives," Reinhold Book Corp., N.Y., 1968, p.9

> NG 90 - 95% NC 5 - 10%

May contain also a small amount of camphor, chalk and a nitrocompound.

"International Critical Tables," Vol. 7, First Ed., McGraw-Hill, N.Y. 1930, p. 489

PETN	85 - 92%
Silicone Oil	8 - 15%
Zn 12-hydroxystearate	0.1 - 3.0%
P. Lingens, Ger. Offer	n. 2,027,709,Dec. 9, 197]

PETN 48% Pb(NO₃)₂ 26% Epicote No. 871 26%

Y. Nomura, Japan 71 22,760, Jun. 29, 1971

PETN 34% Pluracol TP 1540 13% Zeolite 4A 2% Vinyl methoxysilane 2%

F. L. J. D. De Prisque, O. J. Nand, P. O. G. Binet, J. P. A. M. Kehren, Fr. Demande 2,124,038, Oct. 27, 1972

PETN	60%
* Polyurethane	30%
Al ^o	10%

Plasticizers, such as dioctyl azelate; antioxidants such as nonylphenyl phosphite, and catalysts such as iron or lead naphthenate may be also present.

G. F. Roche, J. P. Kehren, Fr. 2,144,983, March 23, 1973

PETN

C-8

	4	AN-Fuel Oil			
	NH4NO3	91.3%			
	NB	6.5%			
	Fuel Oil	2.2%			
W. E. Kirst, C	. A. Woodbury,	U. S. 1,992	,217, Feb.	26, 1935	
	NH4NO3	92%			
	DNT	4%			
	Paraffin	4%			
W. E. Kirst, C	. A. Woodbury,	U.S.1,992	2,217, Feb.	26, 1935	
·····	NH4NO3	70%			
	NaNO3	20%			
	NB	6.5%			
	Paraffin	3.5%			
W. E. Kirst, C	. A. Woodbury,	U. S. 1,992	2,217, Feb.	26, 1935	

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NH4NO3 33.7% $Ca(NO_3)_2$ 42.0% 91.96% н₂0 24.3% 85% Diesel Oil 7.86% N-lauryl-y-hydroxybutyramide 15% H₂0₂ (100%) 0.18%

J. D. Butterworth, Ger. Offen. 2,128,253, Dec. 16, 1971

NH4NO3	85.0%
Diesel Oil	5.5%
Water	8.0%
Guar Gum	0.3%
Silica	0.4%
Expanded polystyrene	0.75%
Na2 ^{CO} 3	0.05%
Borax	trace

2010

W. C. G. Baldwin, S. African 71 04,363, Feb. 11, 1972

NH4N03	96.5%
Fuel Oil	2.0%
Cu naphthenate	0.5%
Kerosene	0.5%
Al powder	0.5%
H. E. Mager, Fr. 2,086,735, Feb.	4, 1972

98%	NH4NO3	
2%	Urea	94%

Fuel Oil 62

C. M. Mason, D. R. Forshey, U. S. 3,708,356, Jan. 2, 1973

Wax-impregnated NH ₄ NO ₃	46.30%
TNT-impregnated NH ₄ NO ₃	32.40%
Water	14.90%
Ethylene glycol	6.10%
Polyacrylamide	0.33%
Arsenite	0.01%
C-10	

Tannic acid	0.05%
Chromate	0.003%

H. W. Sheeran, M. H. Oriard, U. S. 3,717,519, Feb. 20, 1973

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NH4NO3	56%
NaNO3	12%
MeNH2 • HNO3	8%
Co (NO ₃) ₂ •6H ₂ 0	2%
s°	2%

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E. L. Falconer, (F. O. K. Finch, U. S. 3,730,790, May 1, 1973

NH₄NO₃ 95.0% Soybean Oil 3.5% Red phosphorus 1.0% Dehydrated coffee powder 0.5%

The use of the coffee powder was said to have increased the detonation rate and the blasting ability of the compositioning the latter by ~50%.

F. G. Farlan, U. S. 3,733,224, May 15, 1973



ICI Australia Ltd., Fr. Demande 2,144,813, March 23, 1973

Black Powders

KNO₃ 62 - 75.7%S^O 10 - 19.4\% Charcoal 5 - 12\%

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"International Critical Tables," Vol. 7, First Ed., McGraw-Hill, N.Y., 1930, p. 489

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Activated carbon, lu particle size also used in place of charcoal.

K. Lovold, U. S. 3,660,546 May 2, 1972

NaNO3	67.3 - 77.1%
s°	9.4 - 14.3%
Charcoal	8.6 - 22.9%

A. Marshall, "Explosives, Their History, Manufacture, Properties and Tests,"
 Vol. 1, J. and A. Churchill, London, 1917, p. 88

Smokeless Powders
39.5%
59.5%
1.0%
187
77%
4%
1%
······································
10.02
81.47
7.6%
1.0%
43.0%
51.6% (13.2%N)
1.4%
3.25%
0.75%

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Chlorates/perchlorates-Combustibles

 $\frac{\text{Cheddites}}{\text{Aromatic NO}_2 \text{ cpds}} = \frac{14\%}{100}$

"International Critical Tables, 'Vo. 7, First Ed., McGraw-Hill, N.Y., 1930, p. 489

<u>Explosive E</u> - KC20₃ 75.36% Nitronaphthalene 1.3% DNT 17.85% Castor Oil 5.32% H₂0 0.17%

"International Critical Tables," Vol. 7, First Ed., McGraw-Hill, N.Y., 1930, p. 489

Explosive F - KCLO₃ 75.27% Nitrated resin 24.63% H₂0 0.10%

"International Critical Tables," Vol. 7, First Ed., McGraw-Hill, N.Y., 1930, p. 489

KCLO₃ 71.80 - 80.00% Oxamide 5.00 - 13.200% Glycidyl ether of glycerol 6.24 - 11.60% Maleic anhydride < 4.39% Ethylene glycol carbona < 4.39% Diethylene glycol dinitrate < 2.50% Triethylenetetramine < 1.35% (Composition used to inflate safety air bags in automobiles) G. A. Lane, T. E. Dergazarian, R. G. Staudacher, Ger. Offen. 2,240,253, Feb. 22, 1973

C-15

Hydroxylammonium perchlorate	60%	
Polyvinylalcohol	15%	
Al powder	25%	

C. J. Swedenberg, M. J. Cziesla, U. S. 3,697,340, Oct. 10, 1972

KCLO4	30%	
NH 4 ^{NO} 3	40%	
NaNO3	7%	
TNT	15%	
Flour	4%	
Wood-meal	3%	
Jelly*	1%	

* 1 part glycerin and 3.5 parts gelatin.

A. M. Marshall, "Explosives, Their History, Manufacture, Properties and Tests," J. and A. Churchill, London, 1917, p. 384

KCLO ₄	37.2%
NG	22.5%
Collodion cotton	0.8%
Di-and Tri-nitrotoluene	3.5%
Ammonium oxalate	25.0%
Wood meal	11.0%

A. M. Marshall, "Explosives, Their History, Manufacture, Properties and Tests," J. and A. Churchill, London, 1917, p. 385

Photoflash Powders

Ti powder 4	8.01%
ксго _з 2	24.85%
Red phosphorus 2	24.85%
Hydroxyethyl cellulose	1.30%
MgO	0.66%
Na lignosulfonate	0.23%
Na (2-ethylhexyl) sulfate	0.03%
Trichlorophenol	0.04%
s°	0.03%

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J. W. Shaffer, U. S. 3,674,411 July 4, 1972

68.6% LiC20₄ 31.4% NaC20₄

60%

40%

Al powder

(Tetryl used to trigger the above composition.)

H. W. Kruse, B. A. Breslow, R. W. Szypulski, U. S. 3,726,728, April 10, 1973

Match Heads Compositions

Ba (Cl0 ₄) ₂	76 %
Shellac	117
s°	4%
Diatomaceous earth	6%
Animal glue	3Z

T. Yanagisawa, Y. Mega, U. S. 3,634,152, Jan. 11, 1972

KCLO3	40.4%
s°	6.3%
Ground Glass	8.4%
Kieselguhr	3.5%
Powd. asbestos	1.4%
Ti0 ₂	0.7%
Pbs ₂ 0 ₄	1.4%
Glue	37.8%
Pigment	0.1%

Societe Industrielle et Forestiere des Allumettes, Fr. Addn. 2,051,933, May 14, 1971

KC203	36.40%
Water	35.00%
Sand	8.73%
Poly (vinyl alcohol)	5.20%
Diatomaceous earth	4.55%
Sulfur	4.00%
Starch	2.50%
ZnO	1.24%
	C-18

Resorcinol	1.10%
Wood resin	0.64%
Pigment	0.64%

STATES ALL ALL INVESTIGATION

R. R. Martin, J. R. Danner, U. S. 3,650,712, March 21, 1972

ксео _з	61.3%
Glass powder	16.7%
s°	7.9%
Gelatin	5.3%
Quartz powder	4.4%
Corn starch	2.6%
Mica powder	1.3%
K2 ^{Cr20} 7	0.4%
Glyoxal	0.2%

M. Takeda, Japan Kokai 73 23,909, March 28, 1973

Surfactants

Poly(oxyethylene)oleyl ether Poly(oxyethylene)sorbitan monooleate Poly(oxyethylene)nonylphenol Poly(oxyethylene)sorbitan monopalmitate

Compatibility Agents and Softening Point Depressants For Binders

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Phenols Sulfamides (N-ethyl-p-toluenesulfonamide) Polyphenols Nitro and nitroso phenols and polyphenols Partial esters of above phenols

Plasticizers

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Ethylene glycol
Epoxidized oils
Naphthenic acid derivatives
Gums
Liquid resins
Aceryl butyl ricinoleate
Acetyl tributyl citrate
Dioctyl azelate
Dibutyl phthalate

Some Combustibles

Fuel Oil Diesel Oil Light Oil Spindle Oil Turbine Oil Motor Oil Glycerol C₂-C₆ Glycols Kerosine Tetralin Soaps of Al, Co, Cn, Mg, Mn, Ni, Pb, 2n

Water Proofing Agents (May constitute 0.1-5% of the composition)

Paraffin wax Petrolatum Nitrated resins Na, Ca, Zn soaps Sodium silicate Nitro-toluenes Nitronaphthalenes Wood rosin Ester gum Polyurethane Dibutylphthalate Castor oil

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Fuel Sensitizers For NH4NO3

Paraffin wax Fuel oil NG TNT (dissolved in DMF) NB NT Nitroxylenes Nitronaphthalenes Nitrophenols Hydrocarbons Carbohydrates PVA Alcohols (amyl, ethylene glycol, glycerin) Aldehydes Ketones Amides Amines Coal Ammonium thiocyanate Al, Mg, Se, S, Sb, Zr Sulfides, carbides, silicides Urea Lignosulphonates

Freezing Point Depressants

Ethylene glycol dinitrate Dinitrotoluene Nitrotoluene

Gas Formers

Peroxides Acetone NaNO₂ KNO₂ NaHCO₃

Aerating Agents

Fibrous pulps and meals Vermiculite Resin microballoons Perlite Glass microballoons Cork

Structural Types

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323

FUEL SADE 1955

1. Aromatic, Hydrocarbon



- 2. Aromatic, Alchol
 - a) Resorcinol



3. Aromatic, Ester

a) Diethyl Phthalate



-N02

- 4. Aromatic, Nitro
 - a) Nitrobenzene
 - b) Nitronapthalene
 - b) Nitronapthalene NO_2 c) Dinitrotoluene $(NO_2)_2$ d) Trinitrotoluene O_2N NO_2 NO_2

D-4

5. Aromatic, Olefin

- 6. Aliphatic, Hydrocarbon
 - a) Petroleum fractions

7. Aliphatic, Alcohol

- a) Glycerol HOCH2CHOHCH2OH
- b) Ethylene Glycol HOCH₂CH₂OH
- c) Propylene Glycol HOCH₂CHOHCH₃

8. Aliphatic, Alcohol-Ether

- a) Diethylene Glycol HOCH, CH, OCH, CH, OH
- b) Glycidyl ether of glycerol $HOCH_2CHOHCH_2OCH_2CHCH_2$

9. Aliphatic, Ether

- a) Diethyl Carbitol EtOCH₂CH₂OCH₂CH₂OEt
- 10. Aliphatic, Ester

b) Ethylene Glycol Carbonate CH₂O

CH20

D-5

11. Aliphatic, Ketone





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12. Aliphatic, Nitro

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a) Ethylene Glycol Dinitrate 02NOCH2CH20N02

b) Diethylene Glycol Dinitrate 02NOCH2CH2OCH2CH2ONO2

- c) Nitromethane CH₃NO₂
- d) Nitroglycerine 02NOCH2CH(ONO2)CH2ONO2

13. Aliphatic, Amide

a) Formamide HCONH₂

DPAM ()NH

Petroleum Fraction Lowgocents (v.p. at 25°)

Ligroin Fraction

Light oil - 76% benzene (95.2 mm)

15% toluene (28.5 mm)

Karosene Fraction (b.p. 175-325°)

Karosene - C_9 to C_{16} hydrocarbons (4.3 - .01 mm) Dodecane (C_{12}) (0.12 mm) Tetralin (0.4 mm) Napthal@ne (7.45 mm) 1-(2-)-methyl naphthalene Two alkyl derivatives of benzene (?)

Gas oil Fraction (b.p. 250-400°)

Fuel oil, disel oil (C_{14} to C_{26} hydrocarbons)

- estimated v.p., 0.1 to 0.0001 mm

Lubricating oil (b.p. > 400°)

Spindle oil, motor oil, turbine oil (< 10^{-4} mm)

Residue

Paraffin wax (C_{26} to C_{30} n-alkanes) (< 10^{-4} mm)