NON-TRADITIONAL EXPLOSIVES: POTENTIAL DETECTION PROBLEMS

Jimmie C. Oxley

Department of Chemistry
~~New Mexico Institute of Mining and Technology~~
~~Socorro, NM 87801~~
University of Rhode Island
Kingston, RI 02881
joxley@chm.uri.edu

ABSTRACT

Most explosive detection technologies have been focused on nitro-based military explosives because, indeed, they have figured in international terrorist incidents. Not only are they readily available through purchase or theft or from sponsoring states, but methods for home synthesis of TNT, PETN and RDX are widely available. Presently substantial resources are being committed to developing explosive detection technologies to protect commercial aircraft, trains, tunnels, nuclear power plants, etc. against such terrorist threats. Most of the systems now under development target a specific characteristic of military or commercial explosives (e.g. mass density, nitrogen density). However, as counterterrorist measures make traditional explosives more difficult to obtain or more risky to use, we should anticipate terrorists may turn to non-traditional explosives. There are hundreds of energetic compounds and many common explosives which, while they do not meet exacting military demands, would be effective terrorist tools.

Although explosive handbooks list hundreds of explosives, the following discussion focuses on only a handful. These have been chosen because they meet the following criteria.

They are explosives or pyrotechnics that do not follow the classic patterns of military explosives, which new   detection   technologies   are expected to target.

The selected energetic compounds are easily obtainable or   are readily prepared.

This paper will also point out energetic systems that can produce violently exothermic reactions without the aid of traditional initiating systems, such as batteries or detonators. Throughout the reading there are suggestions of modes in which certain of these systems could find use in the hands of terrorist.

OVERVIEW

Terrorist attacks generally fall into three broad categories: assassination; seizure(e.g.highjacking); and explosive destruction of a major asset, usually accompanied by substantial loss of life. The recent Mafia-linked assassinations in Sicily indicate the difficulties of protecting more-or-less private individuals against well-equipped and determined terrorists; this is unlikely to change in the foreseeable future. Seizures or highjackings of embassies, commercial aircraft, cruise ships, etc. have and should continue to decline if existing and emerging countermeasures are implemented in conjunction with sound physical security practices.

(In fact, the increase in attempts to destroy commercial aircraft during the past few years may be due to the improvements in anti-seizure technologies and practices.)

Explosive destruction can be accomplished externally or internally. Examples of external attacks include the use of shoulder fired surface-to-air missiles or mines laid on or under railroad tracks. This threat will not be addressed. Examples of internal attacks include all manner of improvised explosive devices smuggled onto commercial aircraft, into government buildings, etc. This paper will focus on technological developments in the area of internal explosive destruction. This is the area in which the greatest research and development efforts have been focused in recent years. The U.S. Federal Aviation Administration, a world leader in this area, has spent well over $100 million on explosive detection R&D during the past decade, and the pace has been increasing. Furthermore, this is the area in which terrorists may have the greatest opportunities for circumventing the emerging counter-terrorist technologies.
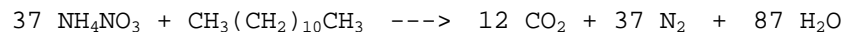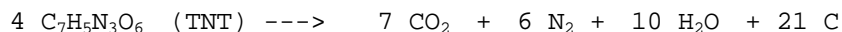
BACKGROUND

An explosion is a rapid expansion of matter into a much greater volume. The expansion is such that the energy is transferred almost completely into mass motion, and thisis accompanied by loud noise and a great deal of heat. Explosive devices may be mechanical, chemical, or atomic. An explosive substance is one which reacts chemically to produce heat and gas and a rapid expansion of matter. A detonation is a very special type of explosion. It is a rapid chemical reaction, initiated by the heat accompanying a shock compression, which liberates sufficient energy, before any expansion occurs, to sustain the shock wave. The shock wave propagates into the unreacted material at supersonic speed, between 1500 and 9000 m/s.

Typical military explosives are organic chemicals; usually they contain only four types of atoms: carbon (C), hydrogen (H), oxygen, (O), and nitrogen (N). To achieve maximum volume change, gas formation, and heat release, explosives are designed to be dense, to have high oxygen content, and to have positive heats of formation. In monomolecular, organic explosives, this means explosives usually contain NO_2 groups. Upon detonation, exothermic reactions occur which transform nitrogen atoms into nitrogen (N_2) gas, while the oxygen atoms combine with the hydrogen and carbon atoms to form the gaseous products H_2O, CO, or CO_2. This is similar to what happens in combustion, but a detonation is different from burning in two ways. In combustion, there is an unlimited amount of oxidizer available.

$$CH_3(CH_2)_nCH_3 \; + \; xs \; O_2 \; \text{-->} \; (n + 2) \; CO_2 + (n + 3) \; H_2O$$
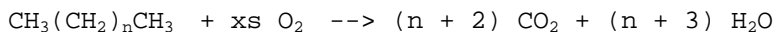
An explosive reacts so quickly that it must have its own source of oxygen near at hand, either in the same molecule, as with most military explosives (e.g. TNT), or in a neighboring molecule, as in the intimate mixture of ammonium nitrate and fuel oil (ANFO).

$$4 \; C_7H_5N_3O_6 \; (TNT) \; \text{--->} \; 7 \; CO_2 + 6 \; N_2 + 10 \; H_2O + 21 \; C$$

$$37 \; NH_4NO_3 + CH_3(CH_2)_{10}CH_3 \; \text{--->} \; 12 \; CO_2 + 37 \; N_2 \; + \; 87 \; H_2O$$

"Oxygen Balance"is a method of quantifying how well an explosive provides its own oxidant. There are various waysof defining oxygen balance (OB). One can balance the oxygen so that every carbon has one oxygen (balanced for CO) or so that every carbon has two oxygen (balanced for CO_2).[1] One can also balance in terms of weight percent oxygen in the explosive (OB) or in terms of oxidant per 100 grams

explosive (OB_{100}):[2]

OB_{100} = [100*($2n_O$ - n_H - $2n_C$ -$2n_{COO}$)]/molecular wt. compound
(balanced to CO)

example: CH_2ONO_2 9 = n_O ; 5 = n_H ; 3 = n_C ; 0 = n_{COO}
  nitroglycerin $CHONO_2$
                  CH_2ONO_2 mol wt. = 9*16 + 5*1 + 3*12 + 3*14 = 227

          OB_{100} = [100*(2*9 – 5 – 2*3 –0)]/227 = (700/227) = 3.08

OB (balanced to CO_2) = [1600*(n_O - $2n_C$ -$.5n_H$)]/molecular wt. compound

  OB nitroglycerin = [1600*(9 – 6 – 5/2)]/227 = 800/227 = 3.52

     The second way in which a detonation differs from a fast burn (deflagration)
is the manner in which the performance is evaluated. The performance of a fuel
is based on the amount of heat it releases; the performance of an explosive has
some relation to the heat it releases, but there is more involved than that. Detonation
is unique in the rapid rate at which energy is released. A high explosive creates
a tremendous power density:

		W/cm^3
Burning acetylene	10^2	
Deflagrating propellant	10^6	
Detonating high explosive	10^{10}	

The performance of an explosive cannot be expressed in a single characteristic.
 Performance is dependent on the detonation rate or velocity, the packing density,
the gas liberated per unit weight, and the heat of explosion. Detonation velocity,
itself, is dependent on packing density, charge diameter, degree of confinement,
and particle size.

     Both the terms brisance and strength are used in describing the performance
of an explosive. When an explosive detonates there is a practically instantaneous
pressure jump from the shock wave. The subsequent expansion of the detonation gases
performs work, moves objects, but it is the pressure jump which shatters or fragments
objects. Brisance (from French for shatter) is a description of the destructive
fragmentation effect of a charge upon its immediate vicinity. Since shattering
effect is dependent upon the suddenness of the pressure rise, it is most dependent
upon detonation velocity. Brisance is the term of importance in military applications.
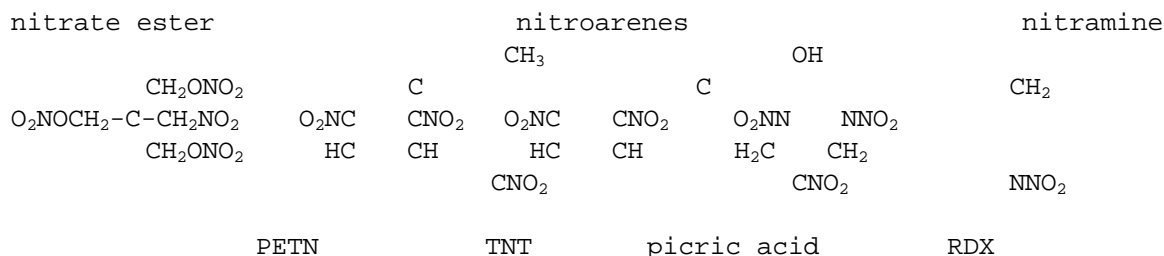 Brisance is often evaluated from detonation velocity, but there are "crusher"
tests in which the compression of lead or copper blocks by the detonation of the
test explosive is taken as a measure of brisance.[1] Strength is important in mining
operations; it describes how much rock can be moved.   The strength of an explosive
is more related to the total gas yield and the heat of explosion. It is often quantified
with the Trauzl lead block test, where ten grams of a test sample are placed in
a $61cm^3$ hole in a lead block and initiated with a No. 8 blasting cap. Performance
is evaluated from the size of the cavity created in the lead block.[3]

Explosives are often classified by the stimuli to which they respond and the degree of response. Propellants or deflagrating or low explosives are combustible materials containing within themselves all oxygen needful for their combustion. Examples are black powder and smokelesspowder (colloided nitrocellulose). Detonating or "high" explosives are characterized by their high rate of reaction and high pressure. In TNT or nitroglycerin, both high explosives, the shock wave travels at a speed of 6000 m/sec, compared to gun powder, a low explosive, in which it travels at ~ 100 m/s.

High explosives are subdivided by the way they are initiated into the designation primary and secondary. Primary explosives are detonated by simple ignition-spark, flame, impact. They do not burn nor even necessarily contain the elements needed to burn. An explosion results whether they are confined or not. Examples of primary explosives are lead azide, lead picrate, lead styphnate, mercury fulminate, m-nitrophenyldiazonium perchlorate, tetracene, nitrogen sulfide (N_4S_4), copper acetylide, fulminating gold, nitrosoguanidine, potassium chlorate with red phosphorus (P_4), and the tartarate and oxalate salts of mercury and silver.

Secondary explosives require a detonator or primary explosive. Secondary explosives differ from primary explosives in not being initiated readily by impact or electrostatic discharge, and they do not easily undergo a deflagration-to-detonation transition (DDT). They can be initiated by large shocks; usually they are initiated by the shock created by a primary explosive. A fuze or blasting cap and frequently a booster are required. (A booster is a sensitive secondary explosive which reinforces the detonation wave from the detonator into the main charge.) Like primary explosives, secondary explosives do not burn, nor do they require confinement. In general, they are more powerful, brisant, than primary explosives. Examples of secondary explosives include nitrocellulose, nitroglycerin, dynamite, TNT, picric acid, tetryl, RDX, HMX, nitroguanidine, ammonium nitrate, ammonium perchlorate, liquid oxygen mixed with wood pulp, fuming nitric acid mixed with nitrobenzene, compressed acetylene and cyanogen.

Military explosives are secondary explosives, and they fall in one of three categories all of which contain nitro NO_2 groups. Nitrate esters, for example, nitroglycerin, nitrocellulose, PETN (active component in DETA sheet), contain $O-NO_2$ groups. These are possibly the oldest explosives still used by the military, nitration of alcohols having become a popular research topic in the 1830's-1840's. Nitroglycerin and nitrocellulose became useful explosives by the 1860's. Nitrate esters are also the least stable military explosives; they lose NO_2 readily, making them relatively easy targets for vapor detection. Nitroarenes with a $C-NO_2$ linkage are typified by TNT (component of Composition B) or picric acid. Nitramines contain $N-NO_2$ groups; typical examples RDX and HMX are often the active components in plastic-bonded explosives such as Composition B, C-4, and Semtex.[4,5]

nitrate ester	nitroarenes		nitramine

$$
\begin{array}{cccc}
 & CH_3 & OH & \\
CH_2ONO_2 & C & C & CH_2 \\
O_2NOCH_2\text{-}C\text{-}CH_2NO_2 \quad O_2NC \quad CNO_2 & O_2NC \quad CNO_2 & O_2NN \quad NNO_2 & \\
CH_2ONO_2 \qquad HC \quad CH & HC \quad CH & H_2C \quad CH_2 & \\
 & CNO_2 & CNO_2 & NNO_2
\end{array}
$$

PETN   TNT picric acid RDX

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1894        1863        1742        1899  discovery
1930        1900  1870                    1940  used
1.67        1.64        1.70        1.77  g/cm³
7975        6942        7480        8639  m/s
1510        1090        1270        1510  cal/g
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DISCUSSION

Present explosive detection technology has focused on military explosives; and, indeed, they have figured in international terrorist incidents. Not only are they readily available for purchase or theft, but methods for home synthesis of TNT,[6] picric acid,[6,7,8] lead picrate,[7,8] PETN[9,10] and RDX[9] are widely available. However, there are hundreds of energetic compounds and many common explosives which, while they do not meet exacting military demands, would be effective terrorist tools. Therefore, as present day interdiction technology becomes more familiar to the public, we should anticipate terrorists may turn to non-military explosives.

Although explosive handbooks[1,3] list hundreds of explosives, the following discussion focuses on only a handful. These have been chosen because they meet at two of the following criteria. They must be explosives or pyrotechnics which do not follow the classic patterns of military explosives, which new detection technologies are expected to target. The selected energetic compounds are easily obtainable or are readily prepared. There is an attempt to point out energetic systems which can produce a violently exothermic reaction without the aid of a traditional initiating system.

Possible non-nitro-explosives can be identified by consulting the propellant, pyrotechnic, and fuel/air explosive literature. Many of these energetic materials can be classed as composite explosives, intimate mixtures of fuels and oxidizers. Peroxides are unique in that they can function as oxidizers in composite explosives or as stand-alone explosives, and triacetone triperoxide has reportedly been used in terrorist incidents. Several self-igniting systems such as boranes, phosphorus, and alkali metals are discussed; for many of these, a blasting cap is not a requirement. In addition to non-nitrogen-containing energetic materials, a number of nitrogen-containing explosives, in which nitrogen is not a part of the conventional nitro-group, will be discussed; included in this class is ammonium nitrate, the most available explosive worldwide.

Civilian Nitrogen-Containing Explosives

Nitromethane CH_3NO_2 is one of the few nitroalkanes which finds occasional applications as an explosive. It is a common industrial solvent and has a unique use as a fuel additive in hobby rockets and race cars. The explosive properties of nitromethane have been extensively studied since it is a relatively simple explosive (heat of explosion 1063 cal/g; detonation velocity 6290 m/s at density 1.138 g/cm^3; lead block test 400 cm^3). Although various propellant and explosive compositions have been patented, and for a time its use as a liquid monopropellant was considered, nitromethane has found no widespread military use. As a blasting agent, gelled nitromethane (gelled with guar gum or nitrocellulose) is comparable to ANFO (ammonium nitrate/fuel oil); it is more difficult to handle, but its higher density produces a high detonation velocity and energy output.[1]

5

The physical properties of nitromethane are such, a clear liquid with boiling point 101°C, melting point -17°C, and density 1.14 g/cc (at 15°C),[4] that it could easily pass as water except for its unique odor (vapor pressure 37 mm at 25°C). However, if nitromethane or a formulation containing it, such as PLX, were bottled, with present detection technology, it would be very difficult to distinguish from water or wine. The drop height of pure nitromethane is relatively low (35 cm), but to detonate it requires a strong initiator. The addition of strong bases and acids (aniline, ethylene diamine, methyl amine, nitric or sulfuric acids) render nitromethane more sensitive to detonation. The methyl protons of nitromethane are acidic, and in the presence of base the anionic salt forms (e.g. $NaCH_2NO_2$). Such salts are much more sensitive than nitromethane itself; therefore, when the intention is to detonate nitromethane, it is usually sensitized with a base.

$$CH_3NO_2 + NaOH \longrightarrow H_2O + CH_2NO_2^- \; Na^+$$

PLX (Picatinny Liquid Explosive), a slightly yellow liquid, contains 95% nitromethane and 5% ethylenediamine.[1] It was developed during World War II for mine clearing operations. It was intended that the two ingredients be mixed just prior to use.
PLX, in a whiskey bottle, and 350 g of Composition C4 in a radio were reportedly used in the downing of Korean Air Flight 858 (November, 1987).

Ammonium Nitrate (AN, NH_4NO_3) is perhaps the most important raw material in the manufacture of industrial explosives (heat of explosion 627 cal/g; detonation velocity 1000-3000 m/s; lead block test 180 cm^3). Prepared by reacting ammonia and nitric acid, it is widely available to the public as a fertilizer.[11] In 1986 over 11 billion pounds of ammonium nitrate were produced in the U.S. Although its end use is mainly fertilizer, almost 20% of it finds use in the explosive industry.[12]

Ammonium nitrate has been used in explosive applications since 1867 when two Swedish chemists patented an explosive which used AN alone or mixed with charcoal, sawdust, naphthalene, picric acid, nitroglycerin, or nitrobenzene. Nobel purchased the invention and used AN in dynamites. Amatol, developed during World War I, was a mixture of AN and TNT in various proportions: 50/50, 60/40, or 80/20. Amatols are not as brisant as TNT; the more AN, the less brisance and the lower the detonation velocity.[13]

	AN	TNT	Al flake	Stearic acid
German	54%	30%	16%	
French	86%		8%	6%

Pure ammonium nitrate is considered an oxidizer rather than an explosive. AN was not considered an explosive until the 1921 disaster in Oppau, Germany, killing almost 600 people. In 1947 two different incidents occurred with ships loaded with fertilizer grade (wax-coated) ammonium nitrate (FEAN). In the first event in Texas City, Texas, the detonation of two ship-loads of AN took about 600 lives; in the second in Brest, France, 20 died. When combustible non-explosives are added to ammonium nitrate, they react with the excess oxygen in AN to produce additional gas and heat, increasing the power and temperature of the explosion. The combustible non-explosive can be rosin, sulfur, charcoal, flour, sugar, oil, or paraffin, but most often it is a fuel oil. ANFO is a mixture of ammonium nitrate with 5-6% fuel oil.

$$37 \; NH_4NO_3 + CH_3(CH_2)_{10}CH_3 \longrightarrow 12 \; CO_2 + 37 \; N_2 + 87 \; H_2O$$
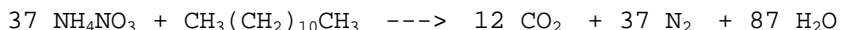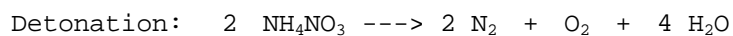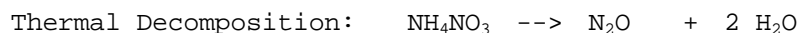
The preparation of ANFO can be as simple as pouring a fuel over a bag of ammonium nitrate. AN may be mixed more intimately with fuel in gels or emulsions. These materials came into use in the mining industry in the 1950's and 1960's, almost completely replacing dynamite. A typical ammonium nitrate aqueous emulsion contains 80% AN, 14% water, and 6% fuel mixed with an emulsifier such as sorbitan monooleate. Such a mixture can be easily whipped up in any kitchen. The hot aqueous ammonium nitrate solution is quickly mixed with the hot fuel/emulsion mixture. To the resulting emulsion, which has the consistency of petroleum jelly, are added some type of hot spot sensitizer--glass microballoons, dinitrogen bubbles, or organic explosive.

AN has a melting point of 170°C and begins to decompose as soon as it melts, the first step being dissociation into ammonia and nitric acid.

$$NH_4NO_3 \longrightarrow NH_3 + HNO_3$$

At low temperature, the rate of decomposition depends on the rate of protonation of nitric acid. As a result, added acidic species, such as ammonium salts or highly charged metal ions, accelerate AN decomposition.[14]
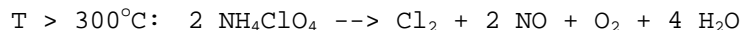
Thermal Decomposition: $\quad NH_4NO_3 \longrightarrow N_2O + 2 H_2O$

Detonation: $\quad 2 NH_4NO_3 \longrightarrow 2 N_2 + O_2 + 4 H_2O$

The availability of ammonium nitrate is such that do-it-at-home explosives books[6,8] list many explosive formulations derived from it, and another such publication[15] labels ANFO as "homemade C-4" and gives detailed instructions as to the proper grade of AN to purchase. Even AN mixed with aluminum is reported to be a powerful explosive.[8]

<u>Ammonium Perchlorate</u> is made by the electrochemical oxidation of sodium chloride NaCl to the chlorate $NaClO_3$ and on to the perchlorate $NaClO_4$. Metathesis with ammonium chloride produces ammonium perchlorate (AP) NH_4ClO_4. Energy-wise this is an expensive process, and both of the U.S. manufactures, Kerr-McGee and WECCO, are located near a hydroelectric dam site. Their combined yearly capacity is about 80 million pounds.[16]

Like ammonium nitrate, ammonium perchlorate (of particle size greater than 45 um) has been classed as an oxidizer rather than as an explosive for purposes of shipping (heat of explosion 488 cal/g; detonation velocity 3400 m/s; lead block test 195 cm^3). If the Texas City disaster of 1947 emphasized the explosive capacity of AN, then the PEPCON detonation of 1988, where half the U.S. AP production capacity was lost and two people were killed, demonstrated the explosive power of AP. Both the French and Germans used ammonium perchlorate explosives during World War I.[13] Since the PEPCON explosion, the TNT equivalence of AP has been measured and found to be about 0.31.

Decomposition of AP is reported to produce NO and nitrous oxide as well as oxygen and chlorine gas; and sublimation is concurrent with decomposition [vapor pressure: log P (mm) = 10.56 - 6283.7/T(K)].[17] As temperature increases, the NO/N_2O ratio increases, and the overall stoichiometry of the reaction changes:[18]

$T < 300^\circ$C: $\quad 4 NH_4ClO_4 \longrightarrow 2 Cl_2 + 2N_2O + 3 O_2 + 8 H_2O$

$T > 300^\circ$C: $\quad 2 NH_4ClO_4 \longrightarrow Cl_2 + 2 NO + O_2 + 4 H_2O$

Mercury Fulminate $Hg(ONC)_2$ is a primary explosive, sensitive to heat, friction, and light (heat of explosion 355 cal/g; detonation velocity 3500 m/s at density 2 g/cm^3). It undergoes marked decomposition above 50°C and is usually stored under water. Until the development of lead azide, mercury fulminate was practically the only explosive used in primers, blasting caps and detonators, either by itself or in composition. Now it has largely been replaced by lead azide or diazodinitrophenol. Used in combination with fuels such as antimony sulfide (Sb_2S_3), mercury fulminate merely deflagrates, but in the presence of $KClO_3$, it can be used to ignite propellants. The synthesis of mercury fulminate is mechanistically complex, but the actual steps are simple enough that the synthesis is included in several do-it-at-home explosives books.[6,8,10] Mercury is dissolved in concentrated nitric acid, ethanol is added, and the white crystals of mercury fulminate formed are thoroughly washed.

$$Hg + HNO_3 \xrightarrow{\text{ethanol}} Hg(ONC)_2$$
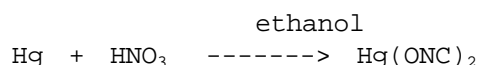
Azides are roughly divided into three classes: stable ionic azides (alkali and alkaline earth azides); unstable covalent azides (haloazides) which frequently explode spontaneously; and heavy-metal azides [$Pb(N_3)_2$, AgN_3] that explode with shock. It is the latter group which is often are used as primers for initiating high explosives. The usual synthetic route is reaction of the metal nitrate with sodium azide.[19]

$$Pb(NO_3)_2 + 2\ NaN_3 \longrightarrow Pb(N_3)_2 + 2\ NaNO_3$$
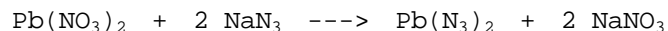
The synthesis of sodium azide has been published so that the terrorist can prepare it and, hence, lead azide in his kitchen.[7] However, sodium azide itself will soon be widely available as it is used in most driver-side air bags; and in many passenger-side air bags up to a half pound is needed. Lead azide has respectable explosive properties (heat of explosion 367 cal/g; detonation velocity 5300 m/s at density 4.6 g/cm^3; lead block test 110 cm^3).

Nitrogen Triiodide NI_3, due to its low brisance and high sensitivity, has no practical use in the energetic materials community.[1] However, it has remained a favorite of teenagers due to its ready synthesis. This is probably the reason its synthesis is also included in the do-it-at-home explosive literature.[6] Iodine crystals are added slowly to concentrated ammonium hydroxide. A brownish-red precipitate forms. The precipitate is filtered and washed with alcohol and ether. This material can be handled only when wet because when dry, the slightest touch, such as a fly, can set it off.

synthesis: $I_2 + NH_3OH \longrightarrow NI_3$

decomposition: $8\ NH_3 \cdot NI_3 \longrightarrow 5\ N_2 + 6\ NH_4I + 9\ I_2$
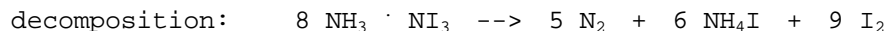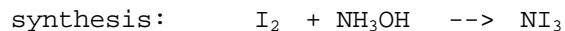
A recent incident during a Hollywood talk show points up the ease with which NI_3 can be prepared and transported. One can envision a cotton sweater saturated with the wet nitrogen triiodide acting as a wireless, metal-less initiator to some more brisant energetic material.

<u>Urea Nitrate</u> Urea nitrate is stable, does not deliquesce, and is a powerful, cool explosive (heat of explosion 796 cal/g; detonation velocity 3400 m/s at density 0.85 g/cm^3; lead block test 270 cm^3). Its disadvantage for military use is that it is corrosively acidic in the presence of moisture.

$$(NH_2)_2-C=O \ + \ HNO_3 \ --> \ (NH_2)_2-C=O \cdot HNO_3$$
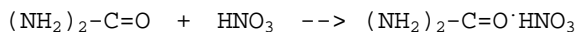
Although this material may be easily detectable, it is included in this listing of terrorist opportunities because it is often cited in the do-it-at-home literature and because the cited starting materials nitric acid and urine are easily obtained.[8] This is probably a good illustration that nitration, practiced on a variety of materials, yields an explosive--sugar, cotton clothing, aluminum foil.

Urea nitrate can be made more powerful by adding aluminum or by drastic dehydration.[7,8] Nitrourea, prepared by dehydration of urea nitrate with concentrated sulfuric acid, is a much more powerful explosive, a nitramine, in fact (heat of explosion 923 cal/g). Nitrourea decomposes in the presence of moisture.

Nitrogen-Free Explosives

A number of potential non-nitrogenous explosives can be identified by consulting the propellant, pyrotechnic, and fuel/air-explosive literature. The boundary between such energetic mixtures is often vague, since the terms propellant, pyrotechnic, and explosive tend to be used to describe end uses rather than chemical composition. A propellant and an explosive can have the same active ingredient. Most of potential non-nitrogenous explosives can be broadly classed as composite explosives. Rather than containing the oxidizer and fuel in a single molecule, as do the organic military explosives, composite explosives are formed by intimately mixing oxidizing compound(s) with fuel(s). These can be pre-mixed or mixed just prior to use. In such mixtures there can be problems due to inhomogeneities; the finer the solid particle size and the more intimate the mix, the better the performance.

A classic example of a composite explosive is black powder, a mixture of the oxidizers KNO_3 and sulfur with the fuel charcoal. As with black powder, the performance of many of these mixtures is related to the degree of confinement. ANFO, a mixture of ammonium nitrate and fuel oil, is another good example of a composite explosive. While military explosives have been common in international terrorism, in domestic terrorism in the U.S. black powder, smokeless powder (nitrocellulose based) and flash powder (KNO_3, $KClO_4$, sulfur) have been the three most common explosive fillers.[20]

The Tables below list oxidizers and fuels which can be combined to form composite explosives. Most contain no nitrogen and are either commercially available or easily prepared.[21]

OXIDIZERS

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oxygen and halogens

perchlorates $KClO_4$ & NH_4, Na, Ba, Ca salts
chlorates $KClO_3$ & Li, Na, Ba salts
hypochlorite $Ca(OCl)_2$

nitrates KNO_3 & NH_4, Na, Ba, Ag, Sr salts

```
chromates     PbCrO₄ & Ba, Ca, K salts
dichromates  K₂Cr₂O₇ & NH₄Cr₂O₇
iodates         KIO₃ & Pb, Ag salts
permanganate KMnO₄

metal oxides BaO₂, Cu₂O, CuO, Fe₂O₃, Fe₃O₄, PbO₂,
             Pb₃O₄, PbO, MnO₂, ZnO

peroxides    Na₂O₂, H₂O₂ (80%), dibenzoylperoxide
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<center>FUELS</center>

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nitrobenzene	petroleum	halogenated-
nitrotoluenes	turpentine	hydrocarbons
nitronaphthalene	naphtha	halogens
nitrocellulose	castor oil	powdered metals
picric acid	sugar	carbon disulfide (CS_2)
	glycerin	phosphorus (P_4)
	acetylene	sulfur (S_8)
	wax, paraffin	
	sawdust	

Good oxidizers have a high oxygen content, and the oxygen is attached to an atom capable of forming a stable lower oxidation state.

$$KClO_4 \; \rightarrow \; KCl + KClO_3$$
$$PbCrO_4 \; \rightarrow \; PbO + CrO_3$$
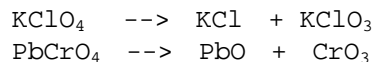
Liquid Oxidizers In 1895 liquid oxygen explosives (LOX) were invented by Linde, who had developed a successful machine for the liquefaction of gases. LOX are formed by impregnating porous combustible materials with liquid oxygen. Lampblack is the absorbent combustible most commonly used. The detonation velocity of the C/O_2 mixture averages 3000 m/s.[22] Twoproblems exist with liquid oxygen containing explosives: they lose their explosiveness as the liquid oxygen evaporates (b.p. -183°C); and they are easily inflamed. Treatment of granular carbonaceous absorbent with aqueous phosphoric acid [or $NH_4(H_2PO_4)$, NH_4Cl, or $(NH_4)_2HPO_4$] resultsin a fireproof absorbent to which liquid oxygen can be added to create an explosive that is non-inflammable by match.[2] During World War I the Germans used LOX when other explosives ran low. In 1926 LOX were used for the first time in commercial rock blasting operations; their use was continued into the 1960's.

Acetylene is a highly flammable gas, but it is also detonable as a gas *vide infra*, as a liquid (boiling point -84°C), or as a solid (melting/freezing point -81°C), acetylene is an explosive. The detonation velocity of solid acetylene is 2270 m/s; combined with liquid oxygen (acetylene 25% / O_2 75%) the detonation velocity is comparable to high explosives (6000 m/s).[1]

$$H-C\equiv C-H + liq \; O_2 \;\; \rightarrow \; 2 \; CO_2 \qquad + \; H_2O$$

Oxygen (boiling point -183^{o}C) can be condensed to a liquid by liquid nitrogen (boiling point -196^{o}C); either could be used to solidify acetylene. Dewar flasks such as thoseused for hot beverage vacuum bottles can contain liquefied oxygen or nitrogen for hours or even days.

Below 21^{o}C nitrogen dioxide (NO_2), a toxic gas, condenses to a colorless liquid, nitrogen tetroxide (N_2O_4). Below -11^{o}C it becomes solid.

$$2 \ NO_2 \ (g) \ <===> \ N_2O_4 \ (liq)$$
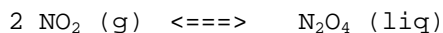
Explosives made with liquid N_2O_4 and combustible liquids (carbon disulfide, nitrobenzene, nitrotoluene, gasoline, halogenated hydrocarbons) were first suggested in 1881 and were generally termed Panclastites. The Germans tested marine torpedoes containing sealed glass containers of N_2O_4 and CS_2 in the 1880's; set-back forces broke the glass containers generating the explosive mixture, and an impact fuze initiated detonation. In World War I, when other explosives were in short supply, the French used Anilites, where liquid N_2O_4 and a fuel were enclosed in separated compartments of a bomb; after the bomb was dropped, passage of air by the nose opened a valve permitting the two liquids to mix.[13] In World War II Panclastites were used in some of the heaviest British aircraft bombs.

Panclastites are inexpensive and easy to prepare; some are more brisant and have better detonation velocities than TNT or picric acid. However, though their performance is favorable, Panclastites are too shock sensitive, too hard to handle, to find common military use. Their extreme sensitivity dictates that they be mixed just prior to use, and the corrosive nature of N_2O_4 requires special vessels. The N_2O_4/fuel mixtures shown below can be absorbed on kieselguhr to form a soft non-plastic material, which has too high a freezing point for military use.
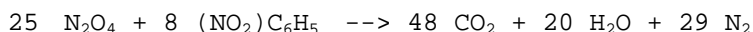
N_2O_4 with carbon disulfide 64/36 has a lead block test of 330 cm^3:

$$3 \ N_2O_4 + 2 \ CS_2 \ --> \ 2 \ CO_2 + 4 \ SO_2 + 3 \ N_2$$

N_2O_4 with benzene 82/18 has a detonation velocity of 6900 m/s:

$$3 \ N_2O_4 + \ C_6H_6 \ --> \ 3 \ CO_2 + 3 \ CO + 3 \ H_2O + 3 \ N_2$$
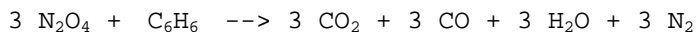
N_2O_4 with nitrobenzene (NB) 70/30 has a detonation velocity of 8000 m/s and a lead block test of 505 cm^3:

$$25 \ N_2O_4 + 8 \ (NO_2)C_6H_5 \ --> \ 48 \ CO_2 + 20 \ H_2O + 29 \ N_2$$

A mixture of 35 parts of carbon disulfide/NB (35/65) with 65 parts N_2O_4 has a lead block test of 435 cm^3. Mixtures of N_2O_4 with 64% nitromethane have a detonation velocity of 6900 m/s.[1]

Nitrogen tetroxide explodes on contact with a number of fuels: acetic anhydride (m.p.-73^{o}C), liquid ammonia (m.p. -78^{o}C), methyl and ethyl nitrate, propene, hydrazine-type fuels. A possible scenario for terrorists would be a sealed ice chest containing two open containers, one of N_2O_4 (m.p. -11^{o}C) and one of methylhydrazine (m.p. -52^{o}C). If these containers were surrounded with dry ice (m.p.-78^{o}C), the oxidizer and fuel should remain solid for sometime. Hours after the terrorists departed the scene, the dry ice would evaporate enough to allow the two components to thaw. When they mixed, an explosion would occur.

Oxides of Chlorine Among the oxides of chlorine, perchlorate is the most stable, but all are energetic and produce toxic fumes. Only chloric and perchloric acids can be isolated. Their reactivity follows that of the salts. They violently react with combustibles, chloric acid being the more reactive.

$$ClO^- \quad < \quad ClO_2^- \quad < \quad ClO_3^- \quad < \quad ClO_4^-$$
hypochlorite chlorite   chlorate   perchlorate
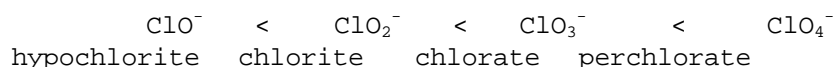
In World War II the U.S. used Galcit propellant that incorporated $KClO_4$ (75%) into molten asphalt (25%).[1,3] It was the precursor of modern composite propellants in which ammonium perchlorate is embedded in a polymer. $KClO_4$, mixed with MnO_2 and a fuel, ignites spontaneously.

Examples of Explosive Mixtures

		Explosives Percentages			squib	primer
$KClO_4$		83	50	75	67	50
$NaNO_3$			30			
dinitrotoluene	12	15				
castor oil		5	5	25		
titanium					33	
zinc						50
aluminum*			+5			

(*Al increases combustion temperature and reduces combustion instabilities.)

Among the oxidizers, chlorates ClO_3^-, are especially hazardous to handle. They decompose exothermically and are sensitive to heat, impact, and friction. The history of chlorate explosives goes back as far as 1788 when Berthollet attempted to make a more powerful gunpowder. A party was organized to witness the manufacture. It included Mr. and Mrs. Lavoisier, the Commissioner of Explosives Chevraud and his daughter, and an engineer Lefort. Berthollet placed a mixture of $KClO_3$, sulfur, and charcoal (6/1/1) in a stamp mill. While the mill was running, the party left the room for breakfast. The first to return to the room, the Commissioner's daughter and the engineer, were killed by an explosion.[13]

Many chlorate mixtures, particularly those which contain sulfur, sulfide, or picric acid are extremely sensitive to blows and friction. The sensitivity can be reduced by phlegmatization in castor oil. Chlorate explosives with aromatic nitro compounds have higher detonation velocities and are more brisant than those in which the carbonaceous material is merely combustible. In 1885, 240,000 lb. of a mixture of $KClO_3$ (79%) and nitrobenzene (21%) along with 42,000lb. dynamite were

used to blast a portion of Hell Gate Channel in New York Harbor. Other similar mixtures are turpentine/phenol (90/10) absorbed on $KClO_3$/MnO_2 (80/20) or nitrobenzene/turpentine (80/20) absorbed on $KClO_3$ /$KMnO_4$ (70/30).

One do-it-at-home explosive book suggests an explosive filler of 9 parts $KClO_3$ and 1 part petroleum jelly or 3 parts $NaClO_3$ to 1 part aluminum or 3 parts $NaClO_3$ to 2 parts sugar.[8] Terrorists improvise, and explosives have been confiscated containing a mixture of $NaClO_3$, aluminum, and petroleum jelly. ($NaClO_3$ is available as a herbicide).

Many mixtures of chlorate with fuels are cap sensitive. Chlorates and perchlorates are used in electric match (squib) compositions. An electric match consists of a metal wire coated with a small bit of heat-sensitive composition. The heat produced by the electrical current in the wire ignites the composition, which initiates the explosive train. Two such compositions are $KClO_3$(55%)/$Pb(SCN)_2$(45%) and $KClO_4$(67%)/Ti(33%). Similar compositions are used in primers, which emit a burst of flame when struck by a firing pin, thus, igniting a propellant: equal amounts of $KClO_3$, Sb_2S_3, and $Pb(N_3)_2$; or $KClO_4$ and Zn.[21]

Examples of Explosive Mixtures

	Percentages					
$KClO_3$	79	80	70	75	83	90
Al					5	
MnO_2		20				
$KMnO_4$			30			
rosin				25	12	
paraffin						10
plus						
turpentine		90	20			
phenol		10				
nitrobenzene (NB)	21		80			

Mixtures of chlorate and fuel will spontaneously ignite with the addition of a drop of concentrated sulfuric acid (H_2SO_4). Spontaneous ignition or explosion can occur when alkali chlorates are combined with very reactive fuels (such as phosphorus, sulfur, powdered arsenic, or selenium) or with moist fuels. In fact, when powdered, dry, unoxidized $KClO_3$ and red phosphorus (Armstrong's powder) are pushed together, they ignite; this reaction has been tamed and utilized by use of separation and a binder in the common safety match. Armstrong's powder, wet with some volatile solvent such as methanol, has been used as an antipersonnel device. It was wrapped in metal foil so that the solvent would evaporate, thus forming a mixture which exploded when an unwary individual picked it up. MnO_2 has been reported as a catalyst for the decomposition of chlorates. Ammonium chlorate NH_4ClO_3 is even more unstable than the potassium salt; therefore, ammonium salts should not be mixed with potassium chlorate.

Calcium hypochlorite [$Ca(OCl)_2$] ignites spontaneously with glycerin. Hypochlorites are generally highly reactive and unstable, but the calcium salt (HTH) is one of the more stable hypochlorites with the abbreviation HTH. Since it is widely used for bleaching and sterilizing, its annual U.S. production is about 10^5 tons. Many forms of hypochlorite are available to the public: as liquid household

bleach (an alkaline solution of NaOCl); as household dish washing detergents and scouring powders [$(Na_3PO_4 \cdot 11\ H_2O)_4 \cdot NaOCl$]; as a liquid bleach for pulp and paper bleaching [a mixture of $Ca(OCl)_2$ and $CaCl_2$]; and as a powdered swimming pool bleach [$Ca(OCl)_2 /CaCl_2/ Ca(OH)_2 \cdot 2H_2O$].

Discussing a mixture of 70% HTH (from a swimming pool supply house) and petroleum naphtha (sold in hardware and paint stores) in a 30/1 ratio, one do-it-at-home book states, "This mixture forms a low power/brisant high explosive which should be used under strong confinement and only as an explosive filler for antipersonnel fragmentation bombs."[8]

Metals Some alkali metals spontaneously ignite on exposure to water or air. As the alkali metals increase in weight, their reaction to air becomes more violent. While potassium may oxidize so rapidly that it melts and ignites when pressure is applied (as in cutting), cesium burns in air as soon as it is removed from an inert oil covering. Moisture in the air serves to enhance further reactivity. Sodium and potassium form a eutectic (NaK) which is spontaneously ignitable. Sodium/potassium alloys are reported to react explosively upon contact with silver halides or to detonate upon contact with halogenated organic materials such as carbon tetrachloride.

Potassium and heavier alkali metals burst into flame upon contact with water. Sodium too will inflame in water if it can be anchored in one spot long enough to allow the heat of reaction to ignite the hydrogen being produced:

$$Na + H_2O \longrightarrow NaOH + 1/2\ H_2.$$
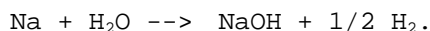
Lithium is the least reactive alkali metal but will ignite if thrown on water as a dispersion. In World War II the Germans used land mines composed of sodium and methyl nitrate in separate compartments. Pressure brought the two together and into action.
Terrorists could cause a lot of excitement by leaving a chuck of potassium in a strategic location covered with a volatile solvent. When the solvent had evaporated, the potassium would react explosively with the atmosphere.

Some finely-divided (powdered) non-alkali metals will also burst into flame in the presence of air. The best known are lead, iron, nickel, cobalt, and aluminum. These can be prepared by pyrolysis of their organic salts or by reduction of their oxides, or in some cases, by formation of a mercury amalgam. These metals may also explosively react with water, halogenated hydrocarbons, and halogens. Recently a large freight truck carrying moist zinc powder exploded as the zinc reacted exothermically with water to form hydrogen.

$$Zn + H_2O \longrightarrow ZnO + H_2$$
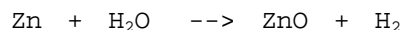
A fatal accident also resulted from the exposure of powdered aluminum to carbon tetrachloride. One do-it-at-home explosives book suggests this syrupy mixture as a cap sensitive explosive; the source of aluminum is the paint store.[8]

$$Al + CCl_4 \longrightarrow AlCl_3$$

$$Fe + xs\ Cl_2 \longrightarrow FeCl_3$$
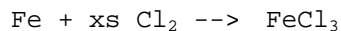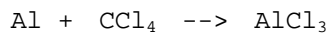
Magnesium is used in a number of pyrotechnics. When a magnesium/silver nitrate mixture is moistened, it reacts explosively. Teflon $(C_2F_4)_n$ with powdered magnesium reacts explosively upon ignition. Devices of this composition are used as decoys for heat-seeking missiles.

$$(C_2F_4)_n + 2n\ Mg \longrightarrow 2n\ C + 2n\ MgF_2$$
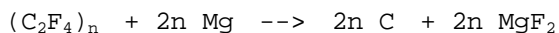
Alkylated Metals Some methyl- and ethyl-substituted metals are spontaneously ignitable in air. The alkylated metals most frequently exhibiting this behavior are the alkali metals (Li, Na), aluminum, zinc, and arsenic or non-metals such as boron and phosphorus. Many of these compounds also react explosively with water and with carbon tetrachloride (CCl_4). It is reported that triethylaluminum [$Al(C_2H_5)_3$] in carbon tetrachloride reacts explosively when warmed to room temperature.

Thermite is generally the redox reaction between a metal oxide and a metal. However, the most important reaction and the one usually referred to by this name is that of aluminum and iron oxide:

$$8\ Al + 3\ Fe_3O_4 \longrightarrow 4\ Al_2O_3 + 9\ Fe$$
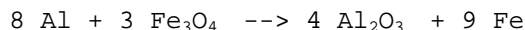
This reaction generates a tremendous amount of heat; molten iron is produced and its melting point is above $1530^{\circ}C$. One peaceful application of this reaction is for welding in shipyards and railroads. In fact one home-military manual[8] cites these as likely places to obtain pre-mixed thermite for incendiary devices.

With $KMnO_4$ in the metal mixture, reaction can be triggered with added glycerol. With sugar in the initial mix, reaction is triggered with a drop of concentrated H_2SO_4. Thermite reactions using CuO or Mn_3O_4 are reported explosive. Mixtures of Pb, PbO_2, and PbO also undergo explosive thermite reactions.

As a result of the extensive compartmentalization required on modern passenger vessels, a very large amount of explosives would be required to sink one. Several carefully distributed thermite charges, however, might be able to burn through a sufficient number of compartments to impair the integrity of even a large and well-maintained vessel.

Peroxides Peroxides, with oxygen in the -1 oxidation state, can be violent oxidizers in the presence of fuel. For example, sodium peroxide Na_2O_2 instantly ignites in the presence of moisture and a fuel (magnesium and sawdust or paper, or sulfur or aluminum). In addition to this feature, peroxides also can undergo a violent self-decomposition. Peroxides, and particularly hydrogen peroxide, may be appealing alternatives to traditional terrorist explosives. Bottled hydrogen peroxide can easily pass as mineral water. Initiation could be as simple as a small time-release capsule of alkaline lead, silver or manganese salts since these catalyze its decomposition.[1,23]

Hydrogen peroxide H_2O_2 is manufactured in large quantities (U.S. production 10^5 metric tons, 1978). Pure peroxide decomposes violently above $80^{\circ}C$; therefore, it is sold as aqueous solutions (27.5%, 35%, 50%, and 70% in water). It is available

at local pharmacies as a 3% solution for use as a disinfectant or as a 40% solution for use as a hair lightener or as a gel to brighten teeth. It can be concentrated by vacuum distillation, or excess water can be "salted out" with diethyl ether.

Peroxide decomposition into water and oxygen can be catalyzed to a violent reaction by Ag, MnO_2, saliva, or HBr:

$$2 \ H_2O_2 \ (l) \ \text{-->} \ 2 \ H_2O \ (g) \ + \ O_2 \ (g)$$
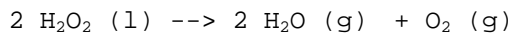
Pure hydrogen peroxide is readily detonable with a heat of explosion of 24.6 kcal/mol. Hydrogen peroxide in concentrations as low as 86% undergo detonation above 50^oC. Solutions of 90.7% peroxide have reported detonation velocities of 5500 to 6000 m/sec. Mixtures of hydrogen peroxide vapor in air with as little as 35 mol% H_2O_2 are reported to detonate at 1 atmosphere with a velocity of 6700 m/sec. Furthermore, hydrogen peroxide, pure or in water, is readily detonable when mixed with organic materials. H_2O_2 / water/ ethanol has a detonation velocity of 6700 m/sec. The violence of the reaction is dependent upon the amount of water present, since water acts as an energy sink for the reaction.[1]

Austria made unsuccessful attempts to use H_2O_2 as an explosive in World War I. In World War II the U.S. Navy used it for propulsion in submarine torpedoes. Peroxide explosives have been successfully used in blasting operations. In addition to its monergolic application, hydrogen peroxide can be used with a number of fuels. Hydrogen peroxide mixed with fuels such as methanol, ethanol, or glycerol showed detonation rates as high as 6700 m/s. One of the propellant systems on the space shuttle uses the combination of hydrogen peroxide and unsymmetrical dimethylhydrazine.
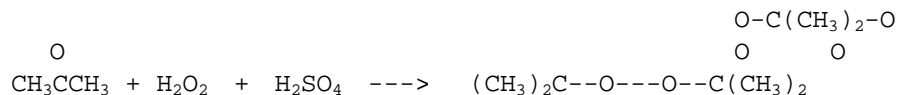
$$8 \ H_2O_2 \ + \ (CH_3)_2NNH_2 \ \text{-->} \ 12 \ H_2O \ (g) \ + \ 2 \ CO_2 \ (g) \ + \ N_2 \ (g)$$
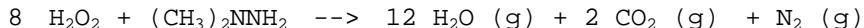
H_2O_2 (60%) with paraformaldehyde forms a crystalline compound of high brisance and sensitive (m.p. 50^oC). Hydrogen peroxide (70%) with diesel fuel and gelling agent also makes a good explosive. H_2O_2 (83%) plus cellulose forms a gelatinous mass which is more powerful than TNT and insensitive to shock or friction. It has an ignition temperature 200^oC; however, it cannot be stored over 48 hours without evolution of peroxide and loss of explosive power. Other patented peroxide explosives include H_2O_2 with water and glycerol, H_2O_2 (70%) with powdered boron (30%), and H_2O_2 used with hexamethylenetetramine and HCl.[1] [Of course, once the would-be terrorist had acquired hexamethylenetetramine (also called hexamine), and he could purchase it as fuel tablets, he might be tempted to nitrate it to make RDX.[9]]
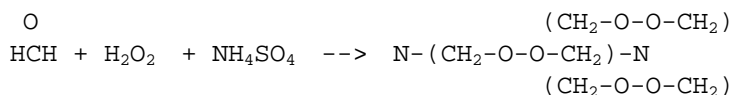
In general, alkyl peroxides tend to be more hazardous than inorganic peroxides. Many alkyl hydroperoxides (ROOH) are reported to explode violently on jarring. Dialkyl peroxides (ROOR) are apparently more shock sensitive. Diacyl peroxides have such notations as "explodes without apparent reason." Dibenzoyl peroxide $C_6H_5COO\text{-}OOCC_6H_5$ is one of the few commercially available alkyl peroxides predictable enough for terrorist use.

Two peroxides can be synthesized from acetone, a dimer and a trimer. The dimer is more difficult to handle, but the trimer, triacetone triperoxide (TATP), is the suspected energetic in several terrorist incidents. The preparation of TATP described in the do-it-at-home explosive literature calls for mixing 30 mL acetone and 50 mL hair bleach (15-25% hydrogen peroxide) and cooling to 5^oC before adding 2.5 mL of sulfuric acid (battery acid).[7,8] The white crystalline solid which forms after standing 24 hours melts at 96^oC.[24] It explodes violently upon heating, impact,

or friction, is highly brisant, very sensitive, and detonable under water. Its
reported detonation velocity is 5290 m/s. It has been suggested for use in primers
and detonator, but due to its volatility and sensitivity it has not found military
application.

$$\begin{array}{c} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O-C(CH_3)_2-O \\ O \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O \quad\quad O \\ CH_3CCH_3 + H_2O_2 + H_2SO_4 \longrightarrow (CH_3)_2C--O---O--C(CH_3)_2 \end{array}$$

   A similarly prepared peroxide described in the do-it-at-home explosive
literature is hexamethylene triperoxide diamine (HMTD).[8] It is prepared from
formaldehyde (40%) and dilute hydrogen peroxide (3%) with ammonium sulfate or by
treating hexamine with 30% hydrogen peroxide and citric acid.[25] It is relatively
unstable and incompatible with most metals; therefore, it finds no military application
as a primary explosive even though its brisance is similar to lead azide.[1]

$$\begin{array}{c} O \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (CH_2-O-O-CH_2) \\ HCH + H_2O_2 + NH_4SO_4 \longrightarrow N-(CH_2-O-O-CH_2)-N \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (CH_2-O-O-CH_2) \end{array}$$


   Fuels In addition to the composite explosives resulting from direct mixing
of the fuels in Table II with the oxidizers in Table I, another class of explosives
should be mentioned. Fuel/air explosives (FAE) involve ignition of fuel droplets
dispersed in air. The first FAE bombs were used in VietNam to clear mine fields
and open helicopter landings. They can produce very large static and dynamic impulses
per weight fuel (since they do not have to carry their own oxygen) and can cause
blast effects over large areas.[1] It has been suggested[26] that FAE might also be
an effective terrorist tool against commercial airlines. Two problems immediately
come to mind. Since most fuels have very limited detonability range, the proportions
of fuel to air must be well calculated.   Furthermore, without human assistance
it is difficult to see how a liquid fuel could be effectively dispersed as an aerosol
in air, while a gaseous fuel would be bulky to transport. However, there are two
fuels that are worth considering in this regard: acetylene and ethylene oxide.
Both are gases at ambient conditions allowing for ease of dispersal, and both have
a very wide detonability range. However, in considering these fuels, it should
be remembered that detonating a FAE requires careful engineering, and it has not
been demonstrated that the right conditions could be achieved in an unmanned luggage
compartment. A more practical use of FAE might be introduction of ethylene oxide
or acetylene into the ventilation system of a large building followed by the timed
detonation of a small device. Acetylene could be easily smuggled into a building
in a portable welding rig, a sufficiently common sight to arouse few suspicions.

   Ethylene oxide is a colorless gas with a wide detonable concentration range
(3% to 100%). The reason it is detonable at any concentration is because oxygen
is already incorporated in the ethylene oxide molecule. However, for complete
combustion it requires additional oxygen from the air or from hydrogen peroxide.

$$\begin{array}{c} O \\ 2 \quad CH_2--CH_2 + 5\ O_2 \longrightarrow 4\ CO_2 + 4\ H_2O \end{array}$$
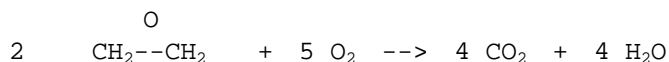
Approximately 6 billion pounds of ethylene oxide were manufactured in the U.S. in

1986, although only about 10% of this is sold off site. Ethylene oxide is easy to

liquefy (boiling point 13.5°C). Under slight pressure, it becomes a liquid with

a density about that of water 0.9 g/mL and can be stored at about the same pressure

as carbonated beverages.

Like ethylene oxide, acetylene is a colorless gas. Acetylene, with a
carbon-carbon triple bond, releases a great deal of energy when these bonds are
broken to combine with oxygen making CO_2. As a result, detonable limits of acetylene
are nearly the same as its flammability limits.[27] Almost any mixture of the gas
is flammable and detonable (from concentrations of 2.5% to 100% in air). Another
advantage of this gas is that it can be generated from a solid, calcium carbide
(density 2.2 g/cm^3). Acetylene can be generated by addition of water or hydrogen
peroxide to calcium carbide (CaC_2):

$$CaC_2 \ + \ 2 \ H_2O \ \text{---}> \ H-C\equiv C-H \ + \ Ca(OH)_2$$
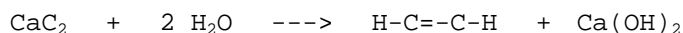
Once formed, the acetylene can be ignited with a hot body, an electrostatic spark,
or shock.

$$H-C\equiv C-H \ + \ 5/2 \ O_2 \ \text{---}> \ 2 \ CO_2 \ + \ H_2O$$
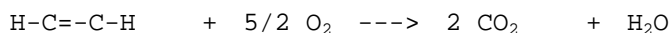
Cyanogen (C_2N_2) is a pungent gas that is easily prepared from mixing solutions
of KCN and $CuSO_4$ or by heating $Hg(CN)_2$. It is used in warfare as a poisonous gas,
but it should not be overlooked that cyanogen is also a high explosive. It explosive
range is wide, from 7% to 73% in air.

Acetylides A number of metal carbides exist which are explosive in their
own right; most are termed acetylides rather than carbides. Copper acetylide and
silver acetylide are most commonly prepared by teenagers. Being primary explosives,
they explode violently upon heating, impact, or friction. Cuprous acetylide is
the only acetylide which has been used in the explosives industry; it has been used
in electric detonators.

Acetylides can be formed by passing acetylene through a solution of the
appropriate metal salt; however, the exact composition of the resulting acetylide
and its performance are dependent upon the salt employed and the reaction conditions.
 Silver acetylide (Ag_2C_2) prepared from bubbling acetylene through an ammoniacal
solution of silver nitrate has a detonation velocity of 1800 m/s, a heat of explosion
of 400 cal/g, and a lead block test of 132 cm^3. If the same reaction were performed
in an aqueous solution, the $AgHC_2 \cdot AgNO_3$ which forms would be less shock sensitive.

Depending on the cupric salt (Cl^-, SO_4^{2-}, NO_3^-) used, cupric acetylide (CuC_2)
is a black amorphous powder which explodes on contact with a drop of nitric acid,
or it is lustrous, metallic platelets which explode upon touch. Cuprous acetylide
(Cu_2C_2) can be formed by passing acetylene through an anaerobic ammoniacal solution

of a cuprous salt; it is also formed whenever acetylene gas comes in contact with copper metal. Mixtures of Cu_2C_2 and lead chlorate ($PbClO_3$) are extremely sensitive to friction. Cu_2C_2 explodes on contact with nitric acid, permanganates, sulfuric acid, or halogens (Br_2 or Cl_2). These facts suggest a terrorist scenario. Terrorist plumbers install a length of copper piping containing CaC_2 in the U-tube portion of a little used sink where water may sit for some time. The water reacts with the calcium carbide forming acetylene which has time to react with the copper pipe to form cuprous acetylide. For the final step, all that is needed is the introduction of a little nitric or sulfuric acid.

    Self-igniting materials Some chemicals are so reactive to the oxygen in air or to water that they spontaneously ignite. Three parameters affect the spontaneity of ignition in air: the dryness of the air, air pressure, and temperature. Most of these chemical systems cannot be classed as explosives, but if sufficient gas pressure and heat are evolved the effect could be catastrophic. A far more important hazard, however, is the use of such devices as wireless, metal-less initiators of a more powerful explosive device.


    Hydrides Phosphines, silanes, and boranes ignite on contact with air. Diphosphine (P_2H_4) a liquid at room temperature, can be made from the reaction of water with solid calcium phosphide (Ca_3P_2), which, in turn, can be formed from lime and red phosphorus. Adding water to calcium phosphide results in a mixture of phosphine and diphosphine, and a violent deflagration ensues. This reaction as been exploited in naval flares.

$$Ca_3P_2 + H_2O \longrightarrow PH_3 + P_2H_4 \longrightarrow \text{deflagrates}$$
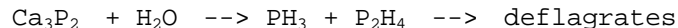
    Only mono- and di-silanes (SiH_4 and Si_2H_6) are stable to air at room temperature. The higher silanes decompose violently:

$$Si_4H_{10} + 13/2\ O_2 \longrightarrow 4\ SiO_2 + 5\ H_2O$$
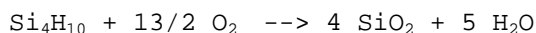
Silane gas is available in large quantities for the manufacture of microelectronic components. Recently an explosion killed three individuals attempting to vent a compressed gas cylinder containing a mixture of silane and nitrous oxide. At room temperature, nitrous oxide N_2O is an inert gas (used as a propellant in spray whipped cream and as a mild anesthetic, laughing gas). However, at elevated temperatures it can act as an oxidizer, in this case, for silane.

$$SiH_4 + N_2O \longrightarrow SiO_2$$
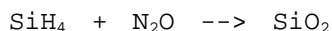
    Diborane (B_2H_6) is a gas available in cylinders or by the action of 85% phosphoric acid on $NaBH_4$. The gas is highly toxic, and, unless it is extremely pure, it reacts with oxygen at room temperature. Borane decomposition in oxygen is extremely exothermic; therefore, boranes, such as decaborane(14) ($B_{10}H_{14}$), have been seriously considered as a component in rocket fuel.

    Phosphorus White phosphorus tends to ignite with slight pressure or by contact with fuel. P_4 self-ignites in air above $34^{\circ}C$; as a result, it is usually stored under water. A solution of white phosphorus in carbon disulfide can be used to

soak a combustible solid, such as paper or cloth. When the CS_2 evaporates, it creates explosive vapors with explosive range (1-50% v/v in air). The finely divided phosphorus left on the combustible material reacts exothermically with the oxygen in air:

$$P_4 + 5\ O_2 \ \ --> \ \ P_4O_{10}$$
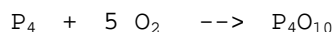
The heat of this reaction initiates the reaction between carbon disulfide and air. Drying of the phosphorus can be delayed by addition of a high-boiling hydrocarbon such as gasoline or toluene.
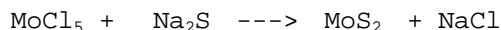
In contrast to white phosphorus, red phosphorus is nontoxic and less sensitive. Red phosphorus bursts into flames or explodes on mild friction or impact in mixture with chlorate, permanganates, lead dioxide (PbO_2), perchlorate, and other active oxidizers ($AgNO_3$).

<u>Miscellaneous Energetics</u> Potassium permanganate and glycerin will ignite spontaneously after a small delay, due to the difficulty in wetting the $KMnO_4$ with viscose glycerin. Ethylene glycol, acetaldehyde, benzaldehyde, or DMSO could be used in place of glycerin. Potassium permanganate and concentrated sulfuric acid can readily inflame when in contact with fuels. $KMnO_4$ was once a common medicine for farm animals:

$$14\ KMnO_4 + 4\ C_3H_5(OH)_3 \ -> \ 7\ K_2CO_3 + 7\ Mn_2O_3 + 5\ CO_2 + 16\ H_2O$$
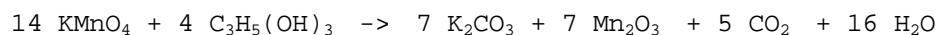
Another self-igniting reaction occurs between $MoCl_5$ and Na_2S:

$$MoCl_5 + \ Na_2S \ ---> \ MoS_2 + NaCl$$

<u>CONCLUSIONS</u>

Present advances in explosive detection technology have either focused on detection of conventional military explosives or on the presence of visually recognizable components. This is an entirely reasonable approach since we have every reason to believe that terrorists bent on destruction will continue to use such dependable, high performance devices until we find a way to stop them. The task of developing effective detectors for small improvised explosive devices has been arduous, and the objective has yet to be fully accomplished. Unfortunately, once we have put such detectors in place, we should prepare to deal with a new generation of devices based on non-military explosives. The range of explosives and the packaging possibilities is staggering. To this also should be added the incendiary devices, which might trigger a more powerful material or which, with proper placement, might prove to be every bit as devastating as an explosive. A "bomb" no longer is a recognizable sphere or pipe, nor does it necessarily need a blasting cap or squib. Every bottle, can of hair spray or shaving cream, every vacuum bottle of coffee is a possible device.

This discussion has been limited to non-military and "exotic" explosive devices. Ignored has been the threat of traditional military explosives, weaponry, biological warfare agents, chemical warfare agents, and fire. However, it should be noted that in most of the systems discussed herein, even if the outcome were not a detonation, a vigorous fire and/or toxic fumes would result. This discussion is intended to provoke new trains of thought on possible terrorist opportunities. While some of the materials considered are thought to be too hazardous for everyday military use,

terrorists may regard the level of risk as acceptable. We know that terrorists learn from their mistakes and ours and that they improvise.   Have terrorists learned from PAN AM 103 that a little properly placed high explosive can be as effective as a large amount?   Then we must learn to more carefully screen our airline ground crews and to ensure that unscreened personnel do not have access to aircraft. Have terrorists learned from the recent explosion in Guadalajara, Mexico that a little pyrotechnic near a large gas line is more effective than a large device? Then we must learn to protect such unguarded targets and to more carefully control the operation of maintenance crews.   Yes, more advanced explosive detection technology must be developed, and non-nitrogenous explosives should be targeted.   But now and in the foreseeable future, profiling, intelligence gathering and analysis, sound physical security practices, and common sense may remain our best security measures.

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Moreover, if the calcium carbide were doped with a little lead or manganese salt,
the basic nature of the resulting calcium hydroxide and the catalytic effect of
the salt would result in a spontaneous and very violent explosion.
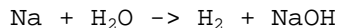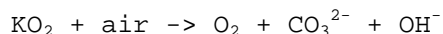
$$CaC_2 + 5\ H_2O_2 \xrightarrow{\ Mn^{2+}\ or\ Pb^{2+}\ } [H\text{-}C\text{=-}C\text{-}H + Ca(OH)_2] \rightarrow 2\ CO_2 + 4\ H_2O$$
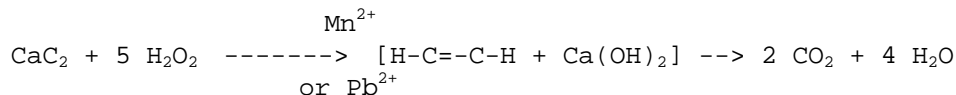
Hypochlorites are manufactured industrially from chlorine oxide; thus, Cl_2O is also
manufactured on a large scale (U.S. production ~10^5 tons). Due to its explosive
character as a liquid or concentrated gas, it is made in low concentrations. It
is a brownish-yellow gas at room temperature, which explodes when heated or sparked
or mixed with ammonia.[1]

KOH/PbO coated with ice as time-capsule.
 barimetric triger could be defeated with vacuum & sniffer
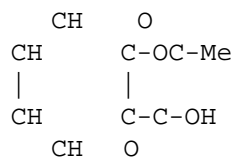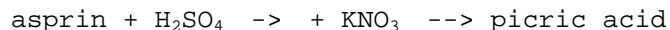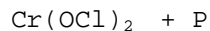$Ca(OCl)_2$ + glycerin or phenol or methyl carbitol (the latter for slow burning)

KO_2 + air -> O_2 + CO_3^{2-} + OH^-
$Na + H_2O \rightarrow H_2 + NaOH$
K covered with ether
KNO_2 + PbO
Chlorox is 5.25% NaOCl

from Field Expedient Methods
asprin + H_2SO_4 -> + KNO_3 --> picric acid

```
   CH    O
CH     C-OC-Me
|      |
CH     C-C-OH
  CH   O
```

$AgNO_3$ + acetonnitrile
$Cr(OCl)_2$ + P

Cl_2 bublled thru turpenine
Two Hell Gate projects
1870's pure, canned NG and also dynamites were used on Halets Point. In 1885
Rack-a-rock, a spengel explosive of chlorate and NB was used on Mill Rock.

$KMnO_4$ poultry water additive, hoof rot, mold, mosquite larvae growth
      Most explosive detection technologies have been focused on nitro-based
explosives; however, there are a number of effective energetic materials which
are not nitro-based and, therefore, are undetectable by these technologies. Many
of these energetic materials can be classed as composite explosives, intimate mixtures

of fuels and oxidizers. Although the possibilities of mixing fuel and oxidizer may seem infinite, many formulations rely on perchlorate or chlorate salts as the oxidizers. Peroxides are unique in that they can function as oxidizers in composite explosives or as stand-alone explosives. The use of hydrogen peroxide as an explosive is the subject of a number of patents, and triacetone triperoxide has reportedly been used in terrorist incidents. Other possible non-nitro-explosives can be identified by consulting the propellant, pyrotechnic, and fuel/air explosive literature. Several self-igniting systems such as boranes, phosphorus, and alkali metals are discussed; for many of these, a blasting cap is not a requirement. In addition to non-nitrogen-containing energetic materials, a number of nitrogen-containing explosives, in which nitrogen is not a part of the conventional nitro-group, will be discussed; included in this class is ammonium nitrate, the most available explosive worldwide.

Guadalajara Mexico April 22, 1992
Pennex leaked gas into main sewer. The night before people complained of smelling gas, but at 9 am the next morning the fire marshall said there was nothing to worry about. At 10:20 am the sewer blew up destroying 600 vehicles, 1422 homes, and 450 businesses. It kelled 206 people.
Source New York time Ap 23, 1992, front page & section 4 May 31.

In Riverside, San Bernadino, a train damaged a pipeline, The next day it blew up killing 4 people (1989)

Mafia hit on Pablo Borsellino in Central Polermo Italy, July 19, 1992.

Nov. 1988 KAL 858 75 mL PLX & 30 G RDX
after Abudaby stop
attempted nitromethane at Frackfurt