# EXPLOSIVES AND PROPELLANTS

## 1. Introduction

When a loud sharp bang is heard similar to a grenade or a bomb exploding it is known as detonation. A deflagration is when the noise is not as loud as that produced by a detonation and is longer in duration and sounds like a hissing sound (ie, the sound of a rocket motor). These effects are generally preceded and accompanied by fire. If a fire is not accompanied by a thundering noise and “blowing up” of a building, it is classed as either burning or combustion. The rate of burning of some explosive materials is relatively slow (few millimeters or centimeters per second) when the explosive is spread on the ground in a thin line. However if these materials are confined, the burn rate will increase and sometimes develop into deflagration or detonation.

## 2. Combustion

Propellants and explosives are both classed as combustible materials and they contain both oxidizer and fuel in their compositions. During combustion propellant and explosive substances will liberate a large amount of gas at high temperatures and will self-sustain combustion without the presence of oxygen in the surrounding atmosphere. The combustion process of propellant and explosive substances can be defined as a self-sustaining exothermic rapid-oxidizing reaction. The chemical composition of propellants and explosives are essentially the same, consequently some propellants can be used as explosives, and some explosives can be used as propellants. Propellants in general generate combustion gases by the deflagration process and the combustion process of propellants is usually subsonic, whereas explosives generate combustion gases by deflagration or detonation. The combustion process of explosives during detonation is supersonic.

**2.1. Deflagrating Explosives.** Deflagrating explosives burn faster and more violently than ordinary combustible materials. They burn with a flame or sparks, or a hissing or crackling noise. Propellants are classified as deflagrating explosives. A small amount of a deflagrating explosive in an unconfined condition will ignite when subjected to a flame, spark, shock, friction or high temperatures.

On initiation local finite “hot spots” are developed either through friction between the solid particulates, by the compression of voids or bubbles in the liquid component, or by plastic flow of the material. These hot spots produce heat and volatile intermediates which then undergo highly exothermic reactions in the gaseous phase, producing more than enough energy and heat to initiate the decomposition and volatilization of newly exposed surfaces. Therefore deflagration is a self-propagating process.

The rate of deflagration increases with increasing degree of confinement. The rate at which the surface of the composition burns, is called the linear burning rate and can be calculated using

$$r = \beta P^{\alpha} \tag{1}$$

where $r$ is the linear burning rate (mm $s^{-1}$), $P$ is the pressure at the surface of the composition at a given instant, $\beta$ is the burning rate coefficient and depends upon the units of $r$ and $P$, and $\alpha$ is the burning rate index which can be found experimentally by burning explosive substances at different pressures $P$ and measuring the linear burning rate $r$. Values for $\alpha$ vary from 0.3 to greater than 1.0.

If a deflagrating explosive is initiated in a confined state (completely enclosed in a casing) the gaseous products will not be able to escape. Hence the pressure will increase with a consequent rapid increase in the rate of deflagration. When the rate of deflagration reaches a velocity of 1000–1800 m $s^{-1}$ it becomes classed as a low order detonation. At a velocity of 5000 m $s^{-1}$ the detonation becomes classed as a high order detonation. Therefore a given explosive may behave as a deflagrating explosive when unconfined and as a detonating explosive when confined and suitably initiated.

The burning of a deflagrating explosive is therefore a surface phenomenon which is similar to other combustible materials except that it does not need a supply of oxygen to sustain the burning. The amount of explosive material burning at the surface in a unit of time depends upon the surface area of the burning surface $A$, its density $\rho$ and the rate at which it is burning $r$. The mass $m$ of the explosive consumed in unit time is given by

$$m = r\,A\,\rho \tag{2}$$

The propagation of an explosion reaction through a deflagrating explosive is therefore based on thermal reactions, these thermal reactions are relatively slow. The explosive material surrounding the initial exploding site is warmed above its decomposition temperature resulting in small explosions. The transfer of energy through the deflagrating explosive is by thermal means through a temperature difference and depends very much on external conditions such as ambient pressure. The speed of the explosion process in deflagrating explosives is always subsonic, that is it is always less than the speed of sound traveling through an explosive material.

**2.2. Detonating Explosives.** Detonating explosives on initiation decompose via the passage of a shockwave rather than thermal processes. The velocity of the shockwave in solid or liquid explosives is between 1500 and 9000 m $s^{-1}$, an order of magnitude higher than that for the deflagration process.

The rate at which the material decomposes is governed by the speed at which the material will transmit the shockwave not by the rate of heat transfer as in deflagrating explosives. The speed of the explosion process in detonating explosives is always supersonic. Detonation can be achieved either by burning to detonation or by an initial shock.

### 2.3. Burning to Detonation.

When an explosive substance is confined in a tube and ignited at one end burning to detonation may take place. The gas generated from the chemical decomposition of the explosive becomes trapped in the tube resulting in an increase in pressure at the burning surface; this in turn raises the linear burning rate. If the linear burning rate is raised so high by pressure pulses generated at the burning surface detonation will take place when it exceeds the velocity of sound. An explosive which burns to detonation will show an appreciable delay between the initiation of burning and the onset of detonation as shown in Figure 1.

This delay will vary according to the nature of the explosive composition, its particle size, density and conditions of confinement.

### 2.4. Shock to Detonation.

Some explosive substances when subjected to a high velocity shockwave can also be detonated. The shockwave forces the particles to compress; this gives rise to adiabatic heating which raises the temperature to above the decomposition temperature of the explosive material. At these high temperatures the explosive crystals undergo an exothermic chemical decomposition which accelerates the shockwave. Detonation will only take place if the velocity of the shockwave in the explosive composition exceeds the velocity of sound. Although initiation to detonation does not take place instantaneously, the delay is negligible being in microseconds.

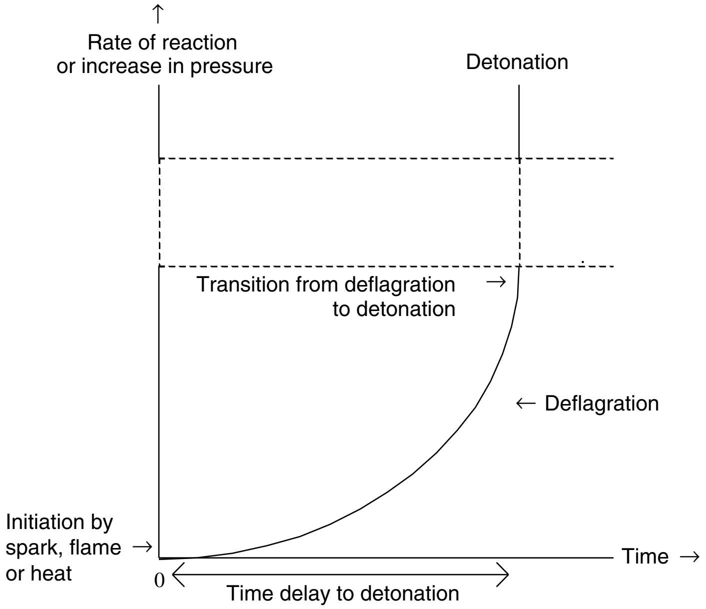


**Fig. 1.** Transition from deflagration to detonation. Reproduced by permission of The Royal Society of Chemistry.

Table 1. **A Comparison of Effects for Deflagrating and Detonating Explosive Materials**

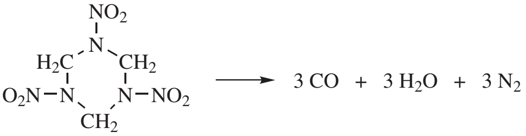
| Deflagrating explosive substances | Detonating explosive substances |
|---|---|
| initiated by flame, sparks, friction, shock, high temperatures | most explosives are capable of detonation if suitably initiated |
| cannot be initiated in the wet state | can be detonated in the wet state |
| oxygen present in formulation | oxygen present in formulation |
| produces long, dull noise accompanied by hissing sound and fire | loud, sharp bang, sometimes accompanied by fire |
| generation of gases used as propulsive forces in propellants | generation of shockwave and used as a destructive force |
| rate of burning is subsonic | rate of burning is supersonic |
| propagation based on thermal reactions | propagation based on shockwave |
| rate of burning increases with ambient pressure | velocity of detonation not affected increasing by increasing ambient pressure |
| not affected by strength of container | velocity of detonation affected by strength of container |
| not dependent on the size of the composition | velocity of detonation dependent on diameter of explosive charge, i.e. critical diameter |
| can convert to detonation if conditions are favourable | does not usually revert to deflagration, if propagation of detonation wave fails explosive composition remains chemically unchanged |

Explosives can therefore be classified by the ease with which they can be ignited and subsequently exploded. Primary explosives are readily ignited or detonated by a small mechanical or electrical stimulus. Secondary explosives are not so easily initiated, they require a high velocity shockwave generally produced from the detonation of a primary explosive. Propellants are generally initiated by a flame, they do not detonate they only deflagrate.

A comparison of effects for deflagrating and detonating explosive materials are presented in Table 1.

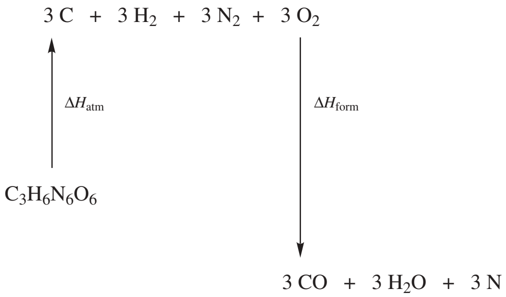
## 3. Explosives

The majority of substances that are classed as explosives generally contain oxygen, nitrogen, and fuels such as carbon and hydrogen. The oxygen is generally attached to nitrogen (ie, NO, $NO_2$, and $NO_3$). Azides, such as lead azide ($PbN_6$), and nitrogen compounds, such as nitrogen triiodide ($NI_3$) and azoimide ($NH_3NI_3$) are the exceptions because they contain no oxygen. In the event of a chemical reaction, the nitrogen and oxygen molecules separate and then unite with the fuel components (carbon and hydrogen) as shown in eq. 3



(3)

During this reaction large quantities of energy are liberated which is generally accompanied by the evolution of hot gases. The heat given out during the reaction is the difference between the heat required to break up the explosive molecule into its elements and the heat released on recombination of these elements to form $CO_2$, $H_2O$, $N_2$ etc, as shown in eq. 4.



(4)

Classification of explosives has been undertaken by many scientists throughout this century. Explosives have been classified with respect to their chemical nature and to their performance and uses. Chemical explosives can be divided into two groups, depending on their chemical nature; those that are classed as substances which are explosive, and those which are explosive mixtures such as blackpowder.

An alternative way of classifying explosives is by their performance and uses. Using this classification, explosives can be divided into three classes; (*1*) primary explosives, (*2*) secondary explosives, and (*3*) propellants as shown in Figure 2.

**3.1. Primary Explosives.** Primary explosives have a high degree of sensitivity to initiation through shock, friction, electric spark, or high temperatures and explode whether they are confined or unconfined. They differ considerably in their sensitivity to heat and in the amount of heat they produce on detonation. Primary explosives differ from secondary explosives in that they undergo a very rapid transition from burning to detonation and have the ability to transmit the

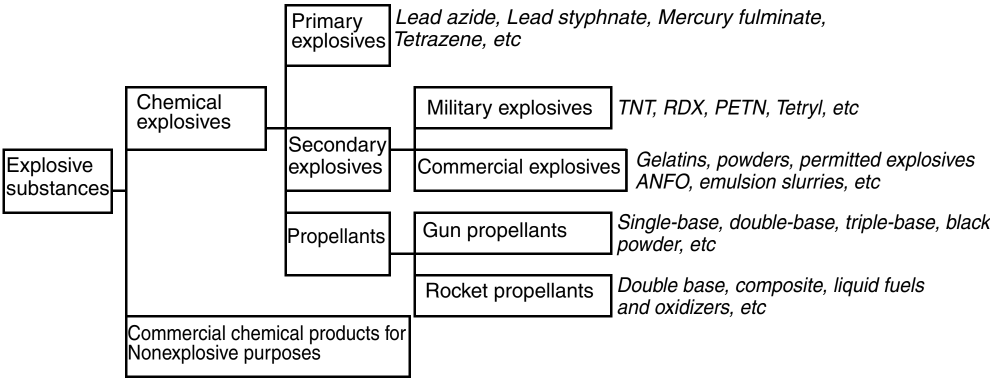


**Fig. 2.** The classes of explosives. Note that pyrotechnic compositions can also be classed as chemical explosives. Reproduced by permission of The Royal Society of Chemistry.

detonation shockwave to less sensitive explosives. On detonation the molecules in the explosive disassociate and produce a tremendous amount of heat and/or shock. This will in turn initiate a second, more stable explosive. For these reasons, they are used in initiating devices. The heat and shock on detonation can vary but is comparable to that for secondary explosives. Their detonation velocities are in the range of 3500–5500 m $s^{-1}$.

**3.2. Secondary Explosives.** Secondary explosives are generally more powerful than primary explosives and can not be detonated readily by heat or shock. Secondary explosives are less sensitive than primary explosives and can only be initiated to detonation by the shock produced by the explosion of a primary explosive. On initiation, the secondary explosive compositions disassociate almost instantaneously into other more stable components.

$$C_3H_6N_6O_6 \longrightarrow 3\ CO + 3\ H_2O + 3\ N_2 \qquad (5)$$

Here the molecular structure of RDX ($C_3H_6N_6O_6$) breaks down on explosion leaving, momentarily, a disorganised mass of atoms. These immediately recombine to give predominantly gaseous products evolving a considerable amount of heat. This only occurs when RDX is stimulated with a primary explosive via a shockwave.

The detonation of the secondary explosive is so fast that a shock wave is generated. This shockwave acts on its surroundings with a great shattering effect (brisance) before the pressure of the expanding gaseous products can take effect. Some secondary explosives can be very stable, rifle bullets can be fired through them or they can be set on fire without detonating. Secondary explosives which detonate at very high velocities exert a much greater force during their detonation that the explosive materials used to initiate them. The values of their detonation velocities are in the range of 5500–9000 m $s^{-1}$ considerably higher than primary explosives.

## 4. Propellants

A propellant is an explosive material which undergoes rapid and predictable combustion (without detonation) resulting in a large volume of hot gas. This gas can be used to propel a projectile, or in gas generators. In order to produce gas quickly a propellant, like a high explosive, must carry its own oxygen together with suitable quantities of fuel elements ie carbon, hydrogen etc. A homogeneous propellant is where the fuel and oxidizer are in the same molecule, ie, nitrocellulose, whereas a heterogeneous propellant has the fuel and oxidizer in separate compounds. Gun propellants are traditionally known to be homogeneous whereas rocket propellants are heterogeneous.

**4.1. Gun Propellants.** The composition of gun propellants have traditionally been fabricated from nitrocellulose based materials. These fibrous materials have good mechanical properties and can be fabricated in granular or stick form (known as grains) to give a constant burning surface without detonation. The size of the propellant grains will depend on the size of the gun. Larger guns require larger grains which take more time to burn. The shape of the propellant grain is also very important. Grains with large surface areas will burn at a faster rate than those with low surface areas. Examples of the different geometrical shapes of propellant grains are shown in Fig. 3.

### 4.2. Compositions.

Apart from the size and shape of the propellant grains, their composition also plays an important role. There exists three basic types of solid gun propellant; these are known as single-base, double-base, and triple-base. Other types of gun propellants which are less common are high energy, liquid and composite gun propellants.

Single-base propellants consist of 90% or more of nitrocellulose. The nitrocellulose is gelled by adding a plasticizer such as carbamite or dibutyl phthalate, and then extruded and chopped into the required grain shape. Double-base propellants contain a mixture of nitrocellulose and nitroglycerine. The energy output is higher than single-base propellants. Triple-base propellants contain nitrocellulose, nitroglycerine, and nitroguanidine. The introduction of about 50% nitroguanidine to the propellant composition results in a reduction in the temperature of the flame and an increase the gas volume. Consequently gun-barrel erosion and muzzle flash are reduced (which is a problem in double-base propellants), and there is also a slight reduction in the performance of the propellant.

In high energy propellants, nitroguanidine is replaced with the explosive RDX in order to increase the velocity of gun propellants. High energy propellants are capable of penetrating armor and are only used in tank guns where very high energies are required. The disadvantage of using high energy propellants is the extensive gun-barrel erosion due to the high flame temperatures, and the vulnerability of the composition to accidental initiation which can lead to detonation. Low vulnerability ammunition (LOVA) propellants contain RDX or HMX, an

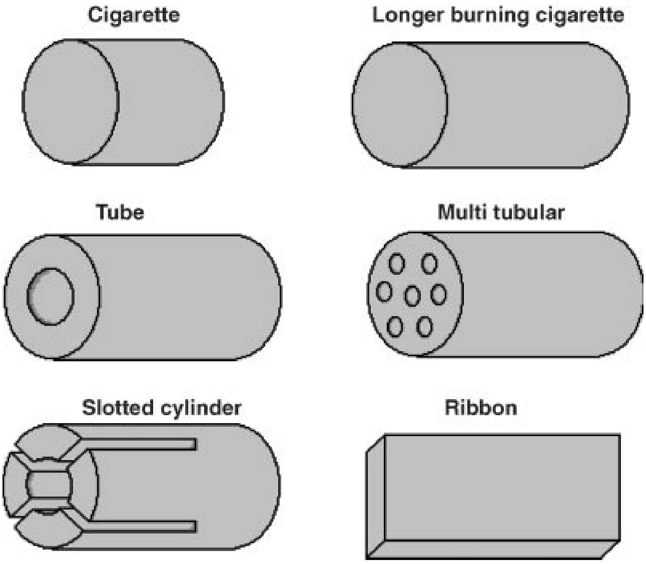


**Fig. 3.** Examples of different geometrical shapes of gun propellants. Reproduced by permission of The Royal Society of Chemistry.

inert polymeric binder and a plasticizer. These composite propellants are less vulnerable to initiation than nitrocellulose-based propellants.

Liquid propellants are light in weight, cheap to produce, less vulnerable to accidental initiation, have a high energy output per unit volume, and a high storage capacity, compared to solid propellants. Considerable research and development has been undertaken in this area and it is estimated that a liquid gun propellant will probably come into service in the 21st century. Liquid gun propellants that are undergoing development are compositions which contain an aqueous (~63%) solution of the crystalline salt hydroxylammonium nitrate (HAN) and a 50:50 mixture of nitromethane and isopropylnitrate.

**4.3. Rocket Propellants.** Rocket propellants are very similar to gun propellants in that they are designed to burn uniformly and smoothly without detonation. Gun propellants however burn more rapidly due to the higher operating pressures in the gun barrel. Rockets propellants are required to burn at a chamber pressure of ~7 MPa compared to ~400 MPa for gun propellant. Rocket propellant must also burn for a longer time to provide a sustained impulse.

**4.4. Composition.** Solid rocket propellants are manufactured in the form of geometrical shapes known as grains. For short range missiles the grains are larger and fewer in number than in a gun cartridge, and are designed to burn over their entire surface to give a high mass burning rate. For larger and longer distance missiles the rocket motor will only contain one or two large grains, as shown in Fig. 4.

Double-base rocket propellants are homogeneous and contain nitrocellulose plasticized with nitroglycerine. Composite rocket propellants are two-phase mixtures comprising of a crystalline oxidizer in a polymeric fuel/binder matrix. The oxidizer is a finely dispersed powder of ammonium perchlorate which is suspended in a fuel. The fuel is a plasticized polymeric material which may have rubbery properties (ie, hydroxy terminated polybutadiene crosslinked with a diisocyanate) or plastic properties (ie, polycaprolactone). Liquid rocket propellants

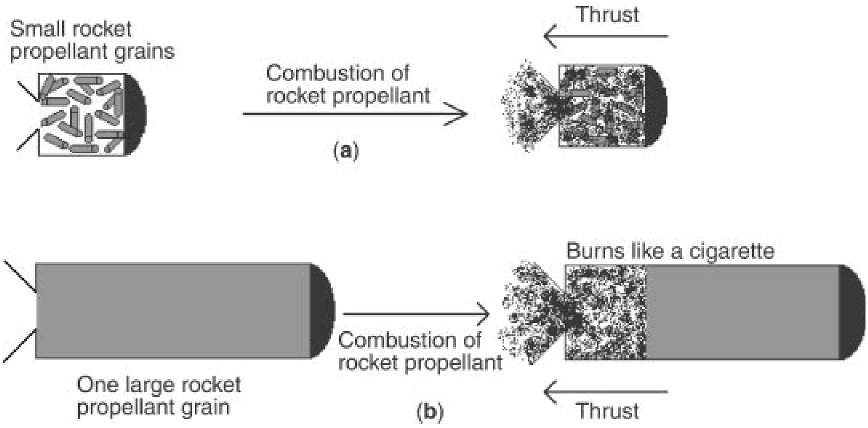


**Fig. 4.** Examples of the geometric structure of rocket propellant for (**a**) short and (**b**) long range missiles. Reproduced by permission of The Royal Society of Chemistry.

are subdivided into monopropellants and bipropellants. Monopropellants are liquids which burn in the absence of external oxygen. They have comparatively low energy and specific impulse and are used in small missiles which require low thrust. Hydrazine is currently the most widely used monopropellant, however hydrogen peroxide, ethylene oxide, isopropyl nitrate, and nitromethane have all been considered or used as monopropellants. Bipropellants consist of two components, a fuel and an oxidizer, that are stored in separate tanks and injected into a combustion chamber where they come into contact and ignite. The fuel component of the bipropellant includes methanol, kerosene, hydrazine, monomethylhydrazine, and unsymmetric dimethylhydrazine (UDMH). Common oxidizers are nitric acid and those based on dinitrogen tetroxide (DNTO). Some bipropellants which are gaseous at room temperature need to be stored and used at low temperatures so that they are in the liquid state. An example of this is the bipropellant hydrogen and oxygen. These types of bipropellants have very high specific impulses and are used on the most demanding missions such as satellite launch vehicles.

**4.5. Gas Generating Propellants.** Solid propellants can be used in systems where large quantities of gas are required in a very short period of time. Such systems include airbags for cars and ejector seats in aircrafts. The advantage of using propellant compositions is the speed at which the gas is generated.

## 5. Chemical Data on Explosive Materials

Specific explosives materials are listed in this section.

### 5.1. Mercury Fulminate

$$(C\equiv NO)_2Hg$$

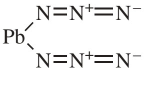
(**1**)

Mercury fulminate [628-86-4] (**1**) is obtained by treating a solution of mercuric nitrate with alcohol in nitric acid. The most important explosive property of mercury fulminate is that after initiation it will easily detonate. On detonation mercury fulminate decomposes to stable products.

$$(CNO)_2Hg \longrightarrow 2\ CO + N_2 + Hg \tag{6}$$

Mercury fulminate is sensitive to impact and friction, and is easily detonated by sparks and flames. It is desensitized by the addition of water but is very sensitive to sunlight and decomposes with the evolution of gas. Some of the properties of mercury fulminate are presented in Table 2.

### 5.2. Lead Azide



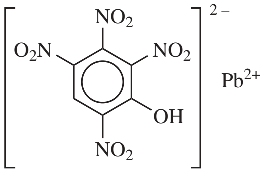
(**2**)

Table 2. **Properties of Compounds (1)–(6)**

| Characteristics | Mercury fulminate (1) | Lead azide (2) | Lead styphnate (3) | Silver azide (4) | Tetrazene (5) | Nitroglycerine (6) |
|---|---|---|---|---|---|---|
| Color | grey, pale brown or white crystalline solid | colorless to white crystalline solid | orange-yellow to dark brown crystalline solid | fine white crystalline solid | light colourless or pale yellow crystalline solid | yellow oil |
| molecular weight | 284.6 | 291.3 | 468.3 | 149.9 | 188.2 | 227.1 |
| decomposition temperature,°C | 90 | 190 | 235 |  | 100 |  |
| melting temperature,°C |  |  |  | 251 |  | 13 |
| thermal ignition temperature,°C | 170 | 327–360 | 267–268 | 273 | 140 | 200 |
| crystal density at 20°C g/cm$^3$ | 4.42 | 4.17, 4.93 | 3.06 | 5.1 | 1.7 | 1.59 |
| energy of formation, kJ/kg | +958 | + 1450 | – 1785 |  | + 1130 | – 1547 |
| enthalpy of formation, kJ/kg | +941 | +1420 | – 1826 |  | + 1005 | – 1633 |

Lead azide [13424-46-9] (**2**) replaced mercury fulminate in detonators. Lead azide has a good shelf life in dry conditions, but is unstable in the presence of moisture, oxidizing agents, and ammonia. It is less sensitive than mercury fulminate to impact, but is more sensitive to friction. Lead azide is widely used in detonators because of its high capacity for initiating other secondary explosives to detonation. Lead azide is superior on a weight basis to mercury fulminate in this role. However, since lead azide is not particularly susceptible to initiation by impact, it is not used alone in initiator components. Instead it is used with lead styphnate and aluminium (ASA mixtures) for military detonators, in a mixture with tetrazene, and in a composite arrangement topped with a more sensitive composition. Lead azide can exist in two allotropic forms; the more stable α-form which is orthorhombic and the β-form which is monoclinic. The α-form is prepared by rapidly stirring a solution of sodium azide with a solution of lead acetate or lead nitrate, whereas the β-form is prepared by slow diffusion of sodium azide in lead nitrate solutions. The β-form has a tendency to revert to the α-form when its crystals are added to a solution containing the α-form crystals or a solution containing a lead salt. If the β-form crystals are left at a temperature of ~160°C they will also convert to the α-form. Some of the properties of lead azide are presented in Table 2.

### 5.3. Lead Styphnate



(**3**)

Lead styphnate (**3**) also known as lead 2,4,6-trinitroresorcinate [15245-44-0], is usually prepared by adding a solution of lead nitrate to magnesium styphnate. Lead styphnate is practically insoluble in water and most organic solvents. It is very stable at room and elevated temperatures (eg, 75°C) and is non hygroscopic.

Lead styphnate is exceptionally resistant towards nuclear radiation and can easily be ignited by a flame or electric spark. It is very sensitive to the discharge of static electricity. Lead styphnate is a weak primary explosive because of its high metal content (44.5%) and therefore is not used in the filling of detonators. It is used in ignition caps, and in the ASA (ie, lead azide, lead styphnate, and aluminium) mixtures for detonators. Some of the properties of lead styphnate is shown in Table 2.

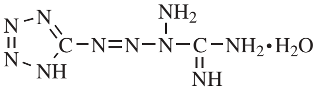
### 5.4. Silver Azide

$$AgN{=}N^{+}{=}N^{-}$$

(**4**)

Silver azide [13863-88-2] (**4**) is manufactured in the same way as lead azide by the action of sodium azide on silver nitrate in an aqueous solution. Silver azide is slightly hygroscopic and is a very vigorous initiator, almost as efficient as lead azide. Like lead azide, silver azide decomposes under the influence of ultraviolet irradiation. If the intensity of radiation is sufficiently high the crystals may explode by photochemical decomposition. The ignition temperature and sensitiveness to impact of silver azide is lower than that of lead azide. Some of the properties of silver azide are presented in Table 2.

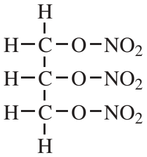
### 5.5. Tetrazene



(**5**)

Tetrazene (**5**) or tetrazolyl guanyltetrazene hydrate [31330-63-9] is slightly hygroscopic and stable at ambient temperatures. It hydrolyzes in boiling water evolving nitrogen gas. The ignition temperature of tetrazene is lower than that for mercury fulminate and it is slightly more sensitive to impact than mercury fulminate. The detonation properties of tetrazene depend on the density of the material, ie, its compaction. Tetrazene will detonate when it is not compacted, but when pressed it produces a weaker detonation. The compaction of tetrazene makes the transition from burning to detonation very difficult. Therefore tetrazene is unsuitable for filling detonators. Tetrazene is used in ignition caps where a small amount of tetrazene is added to the composition to improve its sensitivity to percussion and friction. Some of the properties of tetrazene are given in Table 2.

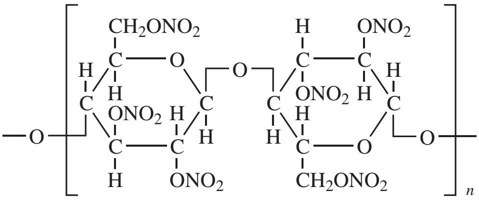
### 5.6. Nitroglycerine



(**6**)

Nitroglycerine, 1,2,3-propanetriol trinitrate, [55-63-0] (**6**) is a very powerful secondary explosive with a high brisance, ie, shattering effect, and it is one of the most important and frequently used components for gelatinous commercial explosives. Nitroglycerine also provides a source of high energy in propellant compositions, and in combination with nitrocellulose and stabilizers, it is the principal component of explosive powders and solid rocket propellants. Nitroglycerine is toxic to handle, causes headaches, and yields toxic products on detonation. It is insoluble in water but readily dissolves in most organic solvents and in a large number of aromatic nitro compounds, and forms a gel with nitrocellulose. The acid-free product is very stable, but exceedingly sensitive to impact. Some of the properties of nitroglycerine are presented in Table 2.

### 5.7. Nitrocellulose



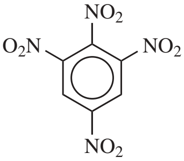
(**7**)

Nitrocellulose [9004-70-0] (**7**) is prepared from cotton are fluffy white solids, which do not melt but ignite in the region of 180°C. They are sensitive to initiation by percussion or electrostatic discharge and can be desensitized by the addition of water. The thermal stability of nitrocellulose decreases with increasing nitrogen content. The chemical stability of nitrocellulose depends on the removal of all traces of acid in the manufacturing process. Cellulose is insoluble in organic solvents, whereas nitrocellulose dissolves in organic solvents to form a gel. The gel has good physical properties due to the polymeric nature of nitrocellulose, and is an essential feature of gun propellants, double-base rocket propellants, gelatin and semi gelatin commercial blasting explosives. Some of the properties of nitrocellulose are presented in Table 3.

Table 3. **Properties of Nitrocellulose (7)**

| Characteristics | Nitrocellulose (7) |
|---|---|
| color | white fibers |
| molecular weight of structural unit | 324.2 (%N/14.14) |
| melting temperature, °C | does not melt |
| thermal ignition temperature, °C | 190 |
| density at 20°C, g/cm$^3$ | 1.67 max value by pressing |
| energy of formation, kJ/kg | |
| 13.3% nitrogen | −2394 |
| 13.0% nitrogen | −2469 |
| 12.5% nitrogen | −2593 |
| 12.0% nitrogen | −2719 |
| 11.5% nitrogen | −2844 |
| 11.0% nitrogen | −2999 |
| enthalpy of formation, kJ/kg | |
| 13.3% nitrogen | −2483 |
| 13.0% nitrogen | −2563 |
| 12.5% nitrogen | −2683 |
| 12.0% nitrogen | −2811 |
| 11.5% nitrogen | −2936 |
| 11.0% nitrogen | −3094 |

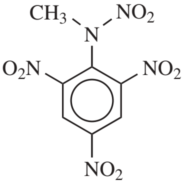
## 5.8. Picric Acid



(**8**)

Picric acid (**8**) also known as 2,4,6-trinitrophenol [88-89-1] is a strong acid, very toxic, soluble in hot water, alcohol, ether, benzene and acetone, and is a fast yellow dye for silk and wool. It attacks common metals, except for aluminium and tin, and produces salts which are very explosive. The explosive power of picric acid is somewhat superior to that of TNT, both as regards to the strength and the velocity of detonation. Picric acid was used in grenade and mine fillings and had a tendency to form impact sensitive metal salts (picrates) with the metal walls of the shells. The filling of mines and grenades was also a hazardous process, since relatively high temperatures were needed to melt the picric acid. Some of the properties of picric acid are presented in Table 4.

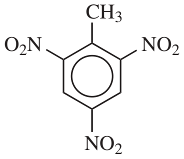
## 5.9. Tetryl



(**9**)

Tetryl (**9**) also known as 2,4,6-trinitrophenylmethylnitramine [479-45-8] is a pale yellow crystalline solid with a melting temperature of 129°C. It is moderately sensitive to initiation by friction and percussion, and is used in the form of pressed pellets as primers for explosive compositions which are less sensitive to initiation. Tetryl is slightly more sensitive than picric acid, and considerably more sensitive that TNT. Tetryl is quite toxic to handle. Some of the properties of tetryl are presented in Table 4.

## 5.10. TNT



(**10**)

Trinitrotoluene, 2-methyl-1,3,5, trinitrobenzene [118-96-7] (**10**) is almost insoluble in water, sparingly soluble in alcohol and will dissolve in benzene, toluene and acetone. It will darken in sunlight and is unstable in alkalis and amines. Some of the properties of TNT are presented in Table 4.

Table 4. **Properties of Compounds (8)–(13)**

| Characteristics | Picric acid (8) | Tetryl (9) | TNT (10) | Nitroguanidine (11) | PETN (12) | RDX (13) |
|---|---|---|---|---|---|---|
| color | yellow crystalline solid | light yellow crystalline solid | pale yellow crystalline solid | white fiber-like crystalline solid | colorless crystalline solid | white crystalline solid |
| molecular weight | 229.1 | 287.1 | 227.1 | 104.1 | 316.1 | 222.1 |
| decomposition temperature, °C |  | 129.5 |  | 232 |  | 213 |
| melting temperature, °C | 122.5 | 130 | 80.8 | 232,[a] 232[b] | 141.3 | 202–204,[c]<br>192–193[d] |
| thermal ignition temperature, °C | 300 | 185 | 300 | 185 | 202 | 260 |
| crystal density at 20°C, g/cm$^3$ | 1.767 | 1.73 | 1.654 | 1.71 | 1.76 | 1.82 |
| energy of formation, kJ/kg | −873.8 | +195.5 | −184.8 | −773.4 | −1509 | +417 |
| enthalpy of formation, kJ/kg | −944.3 | +117.7 | −261.5 | −893.0 | −1683 | +318 |

[a] α-form.

[b] β-form.

[c] Type A.

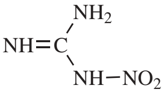
[d] Type B.

TNT has a number of advantages which have made it widely used in military explosives before World War I and up to the present time. These include low manufacturing costs and cheap raw materials, safe to handle, a low sensitivity to impact and friction, and a fairly high explosive power. TNT also has good chemical and thermal stability, low volatility and hygroscopicity, good compatibility with other explosives, a low melting point for casting, and moderate toxicity.

TNT is by far the most important explosive for blasting charges. It is widely used in commercial explosives and is much safer to produce and handle than nitroglycerine and picric acid. A lower grade of TNT can be used for commercial explosives whereas the military grade is very pure. TNT can be loaded into shells by casting as well as pressing. It can be used on its own or by mixing with other components such as ammonium nitrate to give amatols, aluminium powder to give tritonal, RDX to give cyclonite and composition B.

One of the major disadvantages of TNT is the exudation (leaching out) of the isomers dinitrotoluenes and trinitrotoluenes. Even a minute quantity of these substances can result in exudation. This often occurs in the storage of projectiles containing TNT particularly in the summer time. The main disadvantage caused by exudation is the formation of cracks and cavities leading to premature detonation and a reduction in its density. Migration of the isomers to the screw thread of the fuze will form "fire channels". These fire channels can lead to accidental ignition of the charge. If the migrating products penetrate the detonating fuze, malfunctioning of the ammunition components can occur.

### 5.11. Nitroguanidine

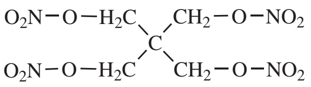


(**11**)

Nitroguanidine [556-88-7] (**11**) is relatively stable below its melting point but decomposes immediately on melting to form ammonia, water vapor and solid products. The gases from the decomposition of nitroguanidine are far less erosive than gases from other similar explosives. Nitroguanidine is soluble in hot water and alkalis, and insoluble in ethers and cold water. It has a high velocity of detonation, a low heat and temperature of explosion, and a high density. Some of the properties of nitroguanidine are given in Table 4.

Nitroguanidine can be used as a secondary explosive but is also suitable for use in flashless propellants as it possesses a low heat and temperature of explosion. These propellants contain a mixture of nitroguanidine, nitrocellulose, nitroglycerine, and nitrodiethyleneglycol which together form a colloidal gel. Nitroguanidine does not dissolve in the gel, but becomes embedded as a fine dispersion. This type of colloidal propellant has the advantage of reducing the erosion of the gunbarrel compared to conventional propellants.

### 5.12. PETN

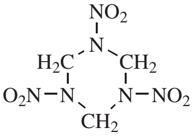


(**12**)

Pentaerythritol tetranitrate, 2,2-bis(hydroxymethyl)-1,3-propanediol tetranitrate [78-11-5] (**12**) is the most stable and the least reactive of the explosive nitric esters. It is insoluble in water, sparingly soluble in alcohol, ether and benzene, and soluble in acetone and methyl acetate. It shows no trace of decomposition when stored for a long time at 100°C. It is relatively insensitive to friction but is very sensitive to initiation by a primary explosive.

PETN is a powerful secondary explosive and has a great shattering effect. It is used in commercial blasting caps, detonation cords and boosters. PETN is not used in its pure form because it is too sensitive to friction and impact. It is therefore usually mixed with plasticized nitrocellulose, or with synthetic rubbers to form polymer bonded explosives (PBXs). PETN can also be incorporated into gelatinous industrial explosives. Some of the properties of PETN are given in Table 4.

### 5.13. RDX

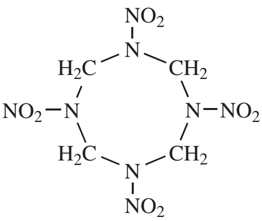


(**13**)

RDX (**13**) also known as hexogen, cyclonite, and cyclotrimethylenetrinitramine [121-82-4] is a white crystalline solid with a melting temperature of 204°C. Pure RDX is very sensitive to initiation by impact and friction and is desensitised by coating the crystals with wax, oils, or grease. It can also be compounded with mineral jelly and similar materials to give plastic explosives. Insensitive explosive compositions containing RDX can be achieved by embedding the RDX crystals in a polymeric matrix. This type of composition is known as a polymer bonded explosive (PBX) and is less sensitive to accidental initiation.

RDX has a high chemical stability and great explosive power compared to TNT and picric acid. It is difficult to dissolve RDX in organic liquids but it can be recrystallized from acetone. It has a high melting point which makes it difficult to use in casting, however, when it is mixed with TNT, which has a low melting temperature, a pourable mixture can be obtained. Some of the properties of RDX are presented in Table 4.

### 5.14. HMX



(**14**)

HMX (**14**) also known as octogen and cyclotetramethylenetetranitramine [2691-41-0], is a white crystalline substance which appears in four different

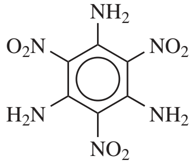
Table 5. **Properties of HMX (14)**

| Characteristics | HMX (14) |
|---|---|
| color | white crystalline solid |
| molecular weight | 296.2 |
| melting temperature, °C | 275 |
| decomposition temperature, °C | 280 |
| thermal ignition temperature, °C | 335 |
| crystal density at 20°C, g/cm$^3$ | |
| $\alpha$-form | 1.87 |
| $\beta$-form | 1.96 |
| $\gamma$-form | 1.82 |
| $\delta$-form | 1.78 |
| energy of formation, kJ/kg | +353.8 |
| enthalpy of formation, kJ/kg | +252.8 |

crystalline forms differing from one another in their density and sensitiveness to impact. The $\beta$-form which is the least sensitive to impact is employed in secondary explosives.

HMX is nonhygroscopic and insoluble in water. It behaves like RDX with respect to its chemical reactivity and solubility in organic solvents. However HMX is more resistant to attack by sodium hydroxide and is more soluble in 55% nitric acid, and 2-nitropropane than RDX. In some instances HMX needs to be separated from RDX and the reactions described above are employed for the separation. As an explosive HMX is superior to RDX in that its ignition temperature is higher and its chemical stability is greater, however the explosive power of HMX is somewhat less than RDX. Some of the properties of HMX are presented in Table 5.

## 5.15. TATB



(**15**)

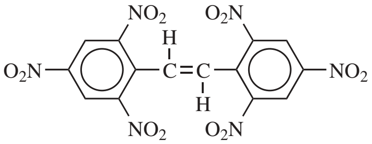
TATB (**15**) is also known as 1,3,5-triamino-2,4,6-trinitrobenzene [3058-38-6] is a yellow-brown colored substance which decomposes rapidly just below its melting temperature. It has excellent thermal stability in the range of 260–290°C and is known as a heat resistant explosive. Some of the properties of TATB are given in Table 6.

The structure of TATB contains many unusual features. The unit cell of TATB consists of molecules arranged in planar sheets. These sheets are held together by strong intra- and intermolecular hydrogen bonding resulting in a graphite like lattice structure with lubricating and elastic properties.

Table 6. **Properties of Compounds (15)–(17)**

| Characteristics | TATB (15) | HNS (16) | NTO (17) |
|---|---|---|---|
| color | yellow-brown crystalline solid | yellow crystalline solid | white |
| molecular weight | 258.1 | 450.1 | 130.1 |
| decomposition temperature, °C | 350 | 318 | 273 |
| melting temperature, °C | 350 | 318 | |
| thermal ignition temperature, °C | 384 | 325 | 258–280 |
| crystal density at 20°C, $g/cm^{-3}$ | 1.93 | 1.74 | 1.93 |
| energy of formation, kJ/kg | −425.0 | +195 | |
| enthalpy of formation, kJ/kg | −597.9 | +128.1 | −901 |
| heat of formation, $kJ/kg^{-1}$ | | | +460–830 |

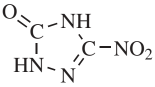
## 5.16. HNS


(**16**)

HNS, hexanitrostilbene [20062-22-0] (**16**) is known as a heat resistant explosive and is also resistant to radiation. It is practically insensitive to an electric spark and is less sensitive to impact than tetryl. Some of the properties of HNS are shown in Table 6.

HNS is used in heat-resistant booster explosives and has been used in the stage separation in space rockets and for seismic experiments on the moon.

**5.17. NTO.** NTO, 5-nitro-1,2,4-triazole-3-one [932-64-9] (**17**) is a new energetic material with attractive characteristics and high performance. It has a high heat of reaction and is less sensitive and more stable than RDX.


(**17**)

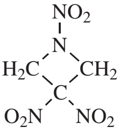
NTO is being developed in many areas these include (*1*) a substitute for ammonium perchlorate or ammonium nitrate in solid rocket propellants, since it does not liberate undesirable products such as HCl and has quite a high burn rate compared to ammonium perchlorate and ammonium nitrate, (*2*) used as a burning rate modifier for composite propellants, (*3*) replacing RDX and HMX in composite solid propellants, and (*4*) improving the performance of gun propellants. Some of the properties of NTO are given in Table 6.

**5.18. TNAZ.** TNAZ is also known as 1,3,3-trinitroazetidine [97645-24-4] (**18**) is reported to be more thermally stable than RDX but more reactive than

Table 7. **Properties of TNAZ**

| Characteristics | TNAZ (18) |
|---|---|
| color | white crystalline solid |
| molecular weight | 192.08 |
| melting temperature, °C | 101 |
| boiling point, °C | 252 |
| crystal density at 20°C, g/cm | 1.84 |
| enthalpy of formation, kJ/kg | +190 |
| heat of melting, kJ/mol | 28–30 |
| heat of sublimation, kJ/mol | +63.22 |
| heat of formation, kJ/mol | +936 |

HMX. Pure TNAZ is more shock sensitive than the explosives based on HMX but less sensitive than analogous PETN. It can be used as a castable explosive and as an ingredient in solid rocket and gun propellant.



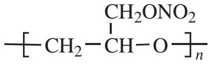
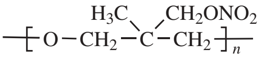
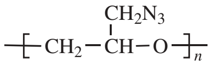
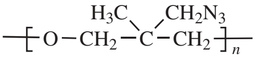
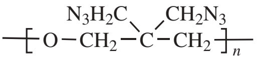
(**18**)

TNAZ is a white crystalline solid and is soluble in acetone, methanol, ethanol, tetrachloromethane and cyclohexane. It has a relatively high vapor pressure and the solidification of its melt is accompanied by a high volume contraction resulting in the formation of shrinkage cavities giving 10–12% porosity. TNAZ exists in two crystal structures; the higher density crystal structure is more stable than the lower density crystal structure. The size of the crystals can be controlled by crystallizing TNAZ from a saturated solution of TNAZ and using an ultra centrifuge, where the formation of defects in the crystal is minimized. An addition of 5–25% wt of a nitroaromatic amine to TNAZ can reduce the shock sensitivity of TNAZ. This is due to the additive acting as nucleation sites for TNAZ when it is crystallised from the melt, resulting in a more homogeneous structure. TNAZ forms eutectic mixtures with some energetic materials. Some properties of TNAZ are shown in Table 7.

## 6. Other Compounds used in Explosive Compositions

There are many other ingredients that are added to explosive compositions which in themselves are not explosive but can enhance the power of explosives, reduce the sensitivity, and aid processing. Aluminium powder is frequently added to explosive and propellant compositions to improve their efficiency. Ammonium nitrate [6484-52-2] is used extensively in commercial explosives and propellants. Small glass or plastic spheres containing oxygen can be added to emulsion slurries to increase its sensitivity to detonation. Polymeric materials

Table 8. **Examples of Energetic Polymers**

| Common name | CAS Registry number | Chemical name | Structure |
|---|---|---|---|
| PolyGLYN | [27814-48-8] | poly(glycidyl nitrate) |  $\left[CH_2-\underset{}{CH}(CH_2ONO_2)-O\right]_n$<br>(**19**) |
| PolyNIMMO | [107760-30-5] | poly(3-nitratomethyl-3-methyl oxetane) |  $\left[O-CH_2-C(H_3C)(CH_2ONO_2)-CH_2\right]_n$<br>(**20**) |
| GAP | [143178-24-9] | glycidyl azide polymer |  $\left[CH_2-CH(CH_2N_3)-O\right]_n$<br>(**21**) |
| PolyAMMO | [94901-15-2] | poly(3-azidomethyl-3- methyl oxetane) |  $\left[O-CH_2-C(H_3C)(CH_2N_3)-CH_2\right]_n$<br>(**22**) |
| PolyBAMO | [81647-83-8] | poly(3,3-bis-azido-methyl oxetane) |  $\left[O-CH_2-C(N_3H_2C)(CH_2N_3)-CH_2\right]_n$<br>(**23**) |

can be added to secondary explosives to produce polymer bonded explosives (PBXs). The polymers are generally used in conjunction with compatible plasticizers to produce insensitive PBXs. The polymers and plasticizers can be in the nitrated form which will increase the power of the explosive. These nitrated forms are known as energetic polymers and energetic plasticizers. Examples of some energetic polymer and plasticizers are presented in Tables 8 and 9 respectively.

Phlegmatizers are added to explosives to aid processing and reduce impact and friction sensitivity of highly sensitive explosives. Phlegmatizers can be waxes which lubricate the explosive crystals and act as a binder.

## 7. Recent Developments

The research into energetic molecules which produce a large amount of gas per unit mass, led to molecular structures which have a high hydrogen to carbon ratio. Examples of these structures are HNF, hydrazinium nitroformate [113595-34-9] and ADN, ammonium dinitramide [140456-78-6]. The majority

Table 9. **Examples of Energetic Plasticizers**

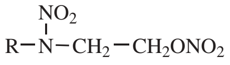
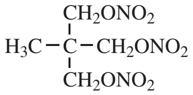
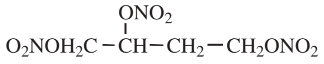
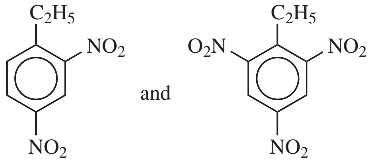
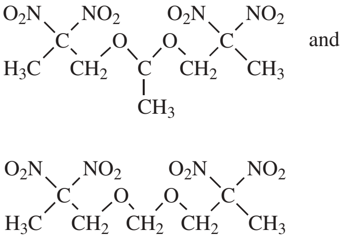
| Common name | CAS Registry number | Chemical name | Structure |
|---|---|---|---|
| NENAs | [17096-47-8],<br>[82486-82-6],<br>[82486-83-7] | alkyl nitratoethyl nitramines |  $R-\overset{NO_2}{N}-CH_2-CH_2ONO_2$ (**24**) |
| EGDN | [628-96-6] | ethylene glycol dinitrate | $O_2NOH_2C-CH_2ONO_2$ (**25**) |
| MTN | [95328-21-5] | metriol trinitrate |  $H_3C-\overset{CH_2ONO_2}{\underset{CH_2ONO_2}{C}}-CH_2ONO_2$ (**26**) |
| BTTN | [6659-60-5] | butane-1,2,4-triol trinitrate |  $O_2NOH_2C-\overset{ONO_2}{CH}-CH_2-CH_2ONO_2$ (**27**) |
| K10 | [31344-57-7],<br>[13985-60-9] | Mixture of di- and tri-nitro ethylbenzene |  (**28**) |
| BDNPA/F | [5917-61-3] | mixture of bis-dinitropropylacetal and bis-dinitropropylformal |  (**29**) |

Table 10. **Examples of Explosive Molecules under Development**

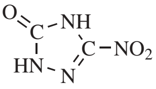
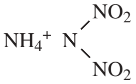
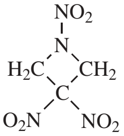
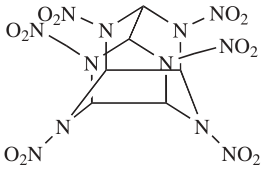
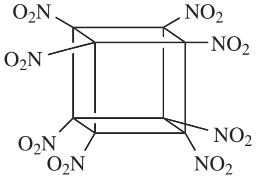
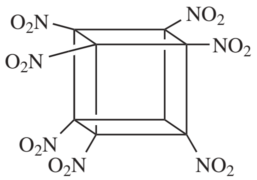
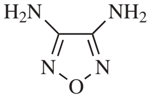
| Common name | CAS Registry number | Chemical name | Structure |
|---|---|---|---|
| NTO | [932-64-9] | 5-nitro-1,2,4-triazol-3-one |  (**30**) |
| ADN | [140456-78-6] | ammonium dinitramide |  $NH_4^+\ N(NO_2)_2$ (**31**) |
| TNAZ | [97645-24-4] | 1,3,3-trinitroazetidine |  (**32**) |
| CL-20 | [135285-90-4] | 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexa-aza tetracyclododecane |  (**33**) |
| HNF | [113595-34-9] | hydrazinium nitroformate | $H_2N{-}NH_2{+}\quad {}^{-}C(NO_2)_3$ (**34**) |
| ONC | [99393-63-2] | octanitrocubane |  (**35**) |

Table 10 (*Continued*)

| Common name | CAS number | Chemical name | Structure |
|---|---|---|---|
| HpNC | [99393-62-1] | heptanitrocubane |  (**36**) |
| DAF | [17220-38-1] | 3,4-diaminofurazan |  (**37**) |

of the development of HNF has been carried out in The Netherlands, whereas the development of ADN has taken place in Russia, United States, and Sweden. ADN is a dense nonchlorine containing powerful oxidizer and is an interesting candidate for replacing ammonium perchlorate as an oxidizer for composite propellants. ADN is less sensitive to impact than RDX and HMX, but more sensitive to friction and electrostatic spark. 2,4,6,8,10,12-Hexanitrohexaazaisowurtzitane [135285-90-4] or HNIW, more commonly called CL20 belongs to the family of high energy dense caged nitramines. CL20 was first synthesized in 1987 by Arnie Nielsen, and is now being produced at SNPE in France in quantities of 50–100 kg in an industrial pilot-scale plant. Octanitrocubane, ONC [99393-63-2] and heptanitrocubane, HpNC [99393-62-1] were successfully synthesized in 1997 and 2000, respectively by Eaton and co-workers. The basic structure of ONC is a cubane molecule where all the hydrogens have been replaced by nitro groups. HpNC is denser than ONC and predicted to be a more powerful, shock-insensitive explosive. Examples of some explosive molecules under development are presented in Table 10.

**7.1. Insensitive Munitions.** Recent developments of novel explosive materials have concentrated on reducing the sensitivity of the explosive materials to accidental initiation by shock, impact, and thermal effects. The explosive materials, which have this reduced sensitivity, are called insensitive munitions, IM. Although these explosive materials are insensitive to accidental initiation they still perform very well when suitably initiated.

**7.2. Pollution Prevention.** Historically waste explosive compositions (including propellants) have been disposed of by dumping the waste composition in the sea, or by burning or detonating the composition in an open bonfire. In 1994 the United Nations banned the dumping of explosive waste into the sea, and due to an increase in environmental awareness burning the explosive waste in an open bonfire will soon be banned since it is environmentally unacceptable. Methods are currently being developed to remove the waste explosive compositions safely from the casing using a high-pressure water jet. The recovered material then has to be disposed; one method is to reformulate the material into a commercial explosive. In the future, when formulating a new explosive composition, scientists must not only consider its overall performance but must make sure that it falls into the “insensitive munitions” category and that it can easily be disposed or recycled in an environmentally friendly manner.

## 8. Acknowledgment

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