

# 1 Introduction to Explosives

## 1.1 Development of Blackpowder

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Blackpowder, also known as gunpowder, was most likely the first explosive composition. In 220 BC an accident was reported involving blackpowder when some Chinese alchemists accidentally made blackpowder while separating gold from silver during a low-temperature reaction. According to Dr Heizo Mambo the alchemists added potassium nitrate [also known as saltpetre ( $\text{KNO}_3$ )] and sulfur to the gold ore in the alchemists' furnace but forgot to add charcoal in the first step of the reaction. Trying to rectify their error they added charcoal in the last step. Unknown to them they had just made blackpowder which resulted in a tremendous explosion.

Blackpowder was not introduced into Europe until the 13th century when an English monk called Roger Bacon in 1249 experimented with potassium nitrate and produced blackpowder, and in 1320 a German monk called Berthold Schwartz (although many dispute his existence) studied the writings of Bacon and began to make blackpowder and study its properties. The results of Schwartz's research probably speeded up the adoption of blackpowder in central Europe. By the end of the 13th century many countries were using blackpowder as a military aid to breach the walls of castles and cities.

Blackpowder contains a fuel and an oxidizer. The fuel is a powdered mixture of charcoal and sulfur which is mixed with potassium nitrate (oxidizer). The mixing process was improved tremendously in 1425 when the Corning, or granulating, process was developed. Heavy wheels were used to grind and press the fuels and oxidizer into a solid mass, which was subsequently broken down into smaller grains.

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The Chemistry of Explosives: 4th Edition

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These grains contained an intimate mixture of the fuels and oxidizer, resulting in a blackpowder which was physically and ballistically superior. Corned blackpowder gradually came into use for small guns and hand grenades during the 15th century and for big guns in the 16th century.

Blackpowder mills (using the Corning process) were erected at Rotherhithe and Waltham Abbey in England between 1554 and 1603.

The first recording of blackpowder being used in civil engineering was during 1548–1572 for the dredging of the River Niemen in Northern Europe, and in 1627 blackpowder was used as a blasting aid for recovering ore in Hungary. Soon, blackpowder was being used for blasting in Germany, Sweden and other countries. In England, the first use of blackpowder for blasting was in the Cornish copper mines in 1670. Bofors Industries of Sweden was established in 1646 and became the main manufacturer of commercial blackpowder in Europe.

## 1.2 Development of Nitroglycerine

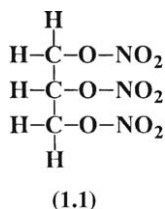
By the middle of the 19th century the limitations of blackpowder as a blasting explosive were becoming apparent. Difficult mining and tunnelling operations required a 'better' explosive. In 1846 the Italian, Professor Ascanio Sobrero discovered liquid nitroglycerine [ $C_3H_5O_3(NO_2)_3$ ]. He soon became aware of the explosive nature of nitroglycerine and discontinued his investigations. A few years later the Swedish inventor, Immanuel Nobel developed a process for manufacturing nitroglycerine, and in 1863 he erected a small manufacturing plant in Helenborg near Stockholm with his son, Alfred. Their initial manufacturing method was to mix glycerol with a cooled mixture of nitric and sulfuric acids in stone jugs. The mixture was stirred by hand and kept cool by iced water; after the reaction had gone to completion the mixture was poured into excess cold water. The second manufacturing process was to pour glycerol and cooled mixed acids into a conical lead vessel which had perforations in the constriction. The product nitroglycerine flowed through the restrictions into a cold-water bath. Both methods involved the washing of nitroglycerine with warm water and a warm alkaline solution to remove the acids. Nobel began to license the construction of nitroglycerine plants which were generally built very close to the site of intended use, as transportation of liquid nitroglycerine tended to generate loss of life and property.

The Nobel family suffered many set-backs in marketing nitroglycerine because it was prone to accidental initiation, and its

initiation in bore holes by blackpowder was unreliable. There were many accidental explosions, one of which destroyed the Nobel factory in 1864 and killed Alfred's brother, Emil. Alfred Nobel in 1864 invented the metal 'blasting cap' detonator which greatly improved the initiation of blackpowder. The detonator contained mercury fulminate  $[\text{Hg}(\text{CNO})_2]$  and was able to replace blackpowder for the initiation of nitroglycerine in bore holes. The mercury fulminate blasting cap produced an initial shock which was transferred to a separate container of nitroglycerine *via* a fuse, initiating the nitroglycerine.

After another major explosion in 1866 which completely demolished the nitroglycerine factory, Alfred turned his attentions to the safety problems of transporting nitroglycerine. To reduce the sensitivity of nitroglycerine Alfred mixed it with an absorbent clay, 'Kieselguhr'. This mixture became known as ghur dynamite and was patented in 1867.

Nitroglycerine (1.1) has a great advantage over blackpowder since it contains both fuel and oxidizer elements in the same molecule. This gives the most intimate contact for both components.



### 1.2.1 Development of Mercury Fulminate

Mercury fulminate was first prepared in the 17th century by the Swedish-German alchemist, Baron Johann Kunkel von Löwenstern.

He obtained this dangerous explosive by treating mercury with nitric acid and alcohol. At that time, Kunkel and other alchemists could not find a use for the explosive and the compound was forgotten until Edward Howard of England rediscovered it between 1799 and 1800. Howard examined the properties of mercury fulminate and proposed its use as a percussion initiator for blackpowder and in 1807 a Scottish Clergyman, Alexander Forsyth patented the device.

### 1.3 Development of Nitrocellulose

At the same time as nitroglycerine was being prepared, the nitration of cellulose to produce nitrocellulose (also known as guncotton) was

also being undertaken by different workers, notably Schönbein at Basel and Böttger at Frankfurt-am-Main during 1845–47. Earlier in 1833, Braconnot had nitrated starch, and in 1838, Pelouze, continuing the experiments of Braconnot, also nitrated paper, cotton and various other materials but did not realize that he had prepared nitrocellulose. With the announcement by Schönbein in 1846, and in the same year by Böttger that nitrocellulose had been prepared, the names of these two men soon became associated with the discovery and utilization of nitrocellulose. However, the published literature at that time contains papers by several investigators on the nitration of cellulose before the process of Schönbein was known.

Many accidents occurred during the preparation of nitrocellulose, and manufacturing plants were destroyed in France, England and Austria. During these years, Sir Frederick Abel was working on the instability problem of nitrocellulose for the British Government at Woolwich and Waltham Abbey, and in 1865 he published his solution to this problem by converting nitrocellulose into a pulp. Abel showed through his process of pulping, boiling and washing that the stability of nitrocellulose could be greatly improved. Nitrocellulose was not used in military and commercial explosives until 1868 when Abel's assistant, E. A. Brown discovered that dry, compressed, highly-nitrated nitrocellulose could be detonated using a mercury fulminate detonator, and wet, compressed nitrocellulose could be exploded by a small quantity of dry nitrocellulose (the principle of a Booster). Thus, large blocks of wet nitrocellulose could be used with comparative safety.

Naval vessels were now able to carry 'guncotton' torpedoes by keeping the major portions of the cargo completely saturated with water.

In 1888 Charles E. Munroe noticed that when a block of guncotton with the manufacturer's name stamped into it was detonated with its lettered surface against a metal plate, the letters were indented into the surface of the plate. If letters were raised in relief above the surface of the guncotton then the letters on the plate would also be raised above its surface. This is now known as the Munroe effect. The Munroe effect refers to the partial focusing of blast energy caused by a hollow or void cut into a piece of explosive.

## 1.4 Development of Dynamite

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In 1875 Alfred Nobel discovered that on mixing nitrocellulose with nitroglycerine a gel was formed. This gel was developed to produce

blasting gelatine, gelatine dynamite and later in 1888, ballistite, the first smokeless powder. Ballistite was a mixture of nitrocellulose, nitroglycerine, benzene and camphor. In 1889 a rival product of similar composition to ballistite was patented by the British Government in the names of Abel and Dewar called 'Cordite'. In its various forms Cordite remained the main propellant of the British Forces until the 1930s.

In 1867, the Swedish chemists Ohlsson and Norrbin found that the explosive properties of dynamites were enhanced by the addition of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). Alfred Nobel subsequently acquired the patent of Ohlsson and Norrbin for ammonium nitrate and used this in his explosive compositions.

### 1.4.1 Development of Ammonium Nitrate

Ammonium nitrate was first prepared in 1654 by Glauber but it was not until the beginning of the 19th century that it was considered for use in explosives by Grindel and Robin as a replacement for potassium nitrate in blackpowder. Its explosive properties were also reported in 1849 by Reise and Millon when a mixture of powdered ammonium nitrate and charcoal exploded on heating.

Ammonium nitrate was not considered to be an explosive although small fires and explosions involving ammonium nitrate occurred throughout the world.

After the end of World War II, the USA Government began shipments to Europe of so-called Fertilizer Grade Ammonium Nitrate (FGAN), which consisted of grained ammonium nitrate coated with about 0.75% wax and conditioned with about 3.5% clay. Since this material was not considered to be an explosive, no special precautions were taken during its handling and shipment – workmen even smoked during the loading of the material.

Numerous shipments were made without trouble prior to 16 and 17 April 1947, when a terrible explosion occurred. The SS Grandchamp and the SS Highflyer, both moored in the harbour of Texas City and loaded with FGAN, blew up. As a consequence of these disasters, a series of investigations was started in the USA in an attempt to determine the possible causes of the explosions. At the same time a more thorough study of the explosive properties of ammonium nitrate and its mixtures with organic and inorganic materials was also conducted. The explosion at Texas City had barely taken place when a similar one aboard the SS Ocean Liberty shook the harbour of Brest in France on 28 July 1947.

The investigations showed that ammonium nitrate was much more dangerous than previously thought and more rigid regulations governing its storage, loading and transporting in the USA were promptly put into effect.

## 1.5 Development of Commercial Explosives

### 1.5.1 Development of Permitted Explosives

Until 1870, blackpowder was the only explosive used in coal mining, and several disastrous explosions occurred. Many attempts were made to modify blackpowder; these included mixing blackpowder with 'cooling agents' such as ammonium sulfate, starch, paraffin, *etc.*, and placing a cylinder filled with water into the bore hole containing the blackpowder. None of these methods proved to be successful.

When nitrocellulose and nitroglycerine were invented, attempts were made to use these as ingredients for coal mining explosives instead of blackpowder but they were found not to be suitable for use in gaseous coal mines. It was not until the development of dynamite and blasting gelatine by Nobel that nitroglycerine-based explosives began to dominate the commercial blasting and mining industries. The growing use of explosives in coal mining brought a corresponding increase in the number of gas and dust explosions, with appalling casualty totals. Some European governments were considering prohibiting the use of explosives in coal mines and resorting to the use of hydraulic devices or compressed air. Before resorting to such drastic measures, some governments decided to appoint scientists, or commissions headed by them, to investigate this problem. Between 1877 and 1880, commissions were created in France, Great Britain, Belgium and Germany. As a result of the work of the French Commission, maximum temperatures were set for explosions in rock blasting and gaseous coal mines. In Germany and England it was recognized that regulating the temperature of the explosion was only one of the factors in making an explosive safe and that other factors should be considered. Consequently, a testing gallery was constructed in 1880 at Gelsenkirchen in Germany in order to test the newly-developed explosives. The testing gallery was intended to imitate as closely as possible the conditions in the mines. A Committee was appointed in England in 1888 and a trial testing gallery at Hebburn Colliery was completed around 1890. After experimenting with various explosives the use of several explosive materials was recommended, mostly based on ammonium nitrate. Explosives which passed the tests were called 'permitted explosives'. Dynamite and blackpowder both

failed the tests and were replaced by explosives based on ammonium nitrate. The results obtained by this Committee led to the Coal Mines Regulation Act of 1906. Following this Act, testing galleries were constructed at Woolwich Arsenal and Rotherham in England.

## 1.5.2 Development of ANFO, Slurry, Emulsion and Blasting Explosives

By 1913, British coal production reached an all-time peak of 287 million tons, consuming more than 5000 tons of explosives annually and by 1917, 92% of these explosives were based on ammonium nitrate. In order to reduce the cost of explosive compositions the explosives industry added more of the cheaper compound ammonium nitrate to the formulations, but this had an unfortunate side effect of reducing the explosives' waterproofness. This was a significant problem because mines and quarries were often wet and the holes drilled to take the explosives regularly filled with water. Chemists overcame this problem by coating the ammonium nitrate with various inorganic powders before mixing it with dynamite, and by improving the packaging of the explosives to prevent water ingress. Accidental explosions still occurred involving mining explosives, and in 1950 manufacturers started to develop explosives which were waterproof and solely contained the less hazardous ammonium nitrate. The most notable composition was ANFO (Ammonium Nitrate Fuel Oil). In the 1970s, the USA companies Ireco and DuPont began adding paint-grade aluminium and monomethylamine nitrate (MAN) to their formulations to produce gelled explosives which could detonate more easily. More recent developments concern the production of emulsion explosives which contain droplets of a solution of ammonium nitrate in oil. These emulsions are waterproof because the continuous phase is a layer of oil, and they can readily detonate since the ammonium nitrate and oil are in close contact. Emulsion explosives are safer than dynamite, and are simple and cheap to manufacture.

The first emulsion explosive was made by Egly and Neckar in 1964 where they mixed a water solution of ammonium nitrate with oil and an emulsifier using a high shear mixer. They then added crystalline ammonium nitrate to the emulsion. This emulsion explosive had a relatively limited lifetime and an improved and stable emulsion explosive called aquaram was later invented by Bluhm in 1969. Bluhm emulsified a hot water solution of ammonium nitrate and sodium nitrate in mineral oil containing an emulsifier and then sensitized the emulsion by either aerating in a high shear mixer, adding a chemical

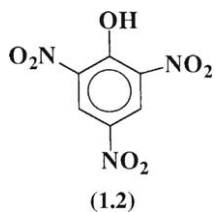
gassing agent or adding hollow glass microballoons. The addition of ANFO to an emulsion explosive to produce a blasting explosive was first prepared by Clay in 1978. The advantage of blasting explosive was that it did not contain sensitizing agents or air bubbles.

## 1.6 Development of Military Explosives

### 1.6.1 Development of Picric Acid

Picric acid [(trinitrophenol) ( $C_6H_3N_3O_7$ )] was found to be a suitable replacement for blackpowder in 1885 by Turpin, and in 1888 blackpowder was replaced by picric acid in British munitions under the name Liddite. Picric acid is probably the earliest known nitrophenol: it is mentioned in the alchemical writings of Glauber as early as 1742. In the second half of the 19th century, picric acid was widely used as a fast dye for silk and wool. It was not until 1830 that the possibility of using picric acid as an explosive was explored by Welter.

Designolle and Brugère suggested that picrate salts could be used as a propellant, while in 1871, Abel proposed the use of ammonium picrate as an explosive. In 1873, Sprengel showed that picric acid could be detonated to an explosion and Turpin, utilizing these results, replaced blackpowder with picric acid for the filling of munition shells. In Russia, Panpushko prepared picric acid in 1894 and soon realized its potential as an explosive. Eventually, picric acid (1.2) was accepted all over the world as the basic explosive for military uses.



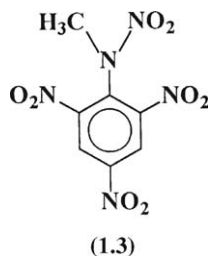
Picric acid did have its problems: in the presence of water it caused corrosion of the shells, its salts were quite sensitive and prone to accidental initiation, and picric acid required prolonged heating at high temperatures in order for it to melt.

### 1.6.2 Development of Tetryl

An explosive called tetryl was also being developed at the same time as picric acid. Tetryl was first prepared in 1877 by Mertens and its structure established by Romburgh in 1883. Tetryl (1.3) was used as

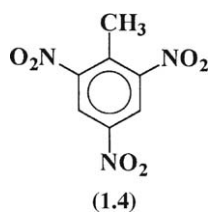


an explosive in 1906, and in the early part of this century it was frequently used as the base charge of blasting caps.



### 1.6.3 Development of TNT

Around 1902 the Germans and British had experimented with trinitrotoluene [(TNT) (C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>6</sub>)], first prepared by Wilbrand in 1863. The first detailed study of the preparation of 2,4,6-trinitrotoluene was by Beilstein and Kuhlberg in 1870, when they discovered the isomer 2,4,5-trinitrotoluene. Pure 2,4,6-trinitrotoluene was prepared in 1880 by Hepp and its structure established in 1883 by Claus and Becker. The manufacture of TNT began in Germany in 1891 and in 1899 aluminium was mixed with TNT to produce an explosive composition. In 1902, TNT was adopted for use by the German Army replacing picric acid, and in 1912 the US Army also started to use TNT. By 1914, TNT (1.4) became the standard explosive for all armies during World War I.



Production of TNT was limited by the availability of toluene from coal tar and it failed to meet demand for the filling of munitions. Use of a mixture of TNT and ammonium nitrate, called amatol, became wide-spread to relieve the shortage of TNT. Underwater explosives used the same formulation with the addition of aluminium and was called aminal.

### 1.6.4 Development of Nitroguanidine

The explosive nitroguanidine was also used in World War I by the Germans as an ingredient for bursting charges. It was mixed with

ammonium nitrate and paraffin for filling trench mortar shells. Nitroguanidine was also used during World War II and later in triple-base propellants.

Nitroguanidine ( $\text{CH}_4\text{N}_4\text{O}_2$ ) was first prepared by Jousselin in 1877 and its properties investigated by Vieille in 1901. In World War I nitroguanidine was mixed with nitrocellulose and used as a flashless propellant. However, there were problems associated with this composition; nitroguanidine attacked nitrocellulose during its storage. This problem was overcome in 1937 by the company Dynamit AG who developed a propellant composition containing nitroguanidine called 'Gudol Pulver'. Gudol Pulver produced very little smoke, had no evidence of a muzzle flash on firing, and was also found to increase the life of the gun barrel.

After World War I, major research programmes were inaugurated to find new and more powerful explosive materials. From these programmes came cyclotrimethylenetrinitramine [(RDX) ( $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ )] also called Cyclonite or Hexogen, and pentaerythritol tetranitrate [(PETN) ( $\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$ )].

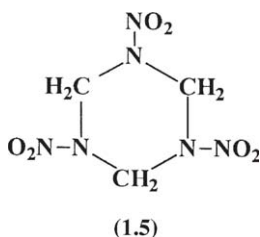
### 1.6.5 Development of PETN

PETN was first prepared in 1894 by nitration of pentaerythritol. Commercial production of PETN could not be achieved until formaldehyde and acetaldehyde required in the synthesis of pentaerythritol became readily available about a decade before World War II. During World War II, RDX was utilized more than PETN because PETN was more sensitive to impact and its chemical stability was poor. Explosive compositions containing 50% PETN and 50% TNT were developed and called 'Pentrolit' or 'Pentolite'. This composition was used for filling hand and anti-tank grenades, and detonators.

### 1.6.6 Development of RDX and HMX

RDX was first prepared in 1899 by the German, Henning for medicinal use. Its value as an explosive was not recognized until 1920 by Herz. Herz succeeded in preparing RDX by direct nitration of hexamine, but the yields were low and the process was expensive and unattractive for large scale production. Hale, at Picatinny Arsenal in 1925, developed a process for manufacturing RDX which produced yields of 68%. However, no further substantial improvements were made in the manufacture of RDX until 1940 when Meissner developed a continuous method for the manufacture of RDX, and Ross and

Schiessler from Canada developed a process which did not require the use of hexamine as a starting material. At the same time, Bachmann developed a manufacturing process for RDX (1.5) from hexamine which gave the greatest yield.



Bachmann's products were known as Type B RDX and contained a constant impurity level of 8–12%. The explosive properties of this impurity were later utilized and the explosive HMX, also known as Octogen, was developed. The Bachmann process was adopted in Canada during World War II, and later in the USA by the Tennessee–Eastman Company. This manufacturing process was more economical and also led to the discovery of several new explosives. A manufacturing route for the synthesis of pure RDX (no impurities) was developed by Brockman, and this became known as Type A RDX.

In Great Britain the Armament Research Department at Woolwich began developing a manufacturing route for RDX after the publication of Herz's patent in 1920. A small-scale pilot plant producing 75 lbs of RDX per day was installed in 1933 and operated until 1939. Another plant was installed in 1939 at Waltham Abbey and a full-scale plant was erected in 1941 near Bridgwater. RDX was not used as the main filling in British shells and bombs during World War II but was added to TNT to increase the power of the explosive compositions. RDX was used in explosive compositions in Germany, France, Italy, Japan, Russia, USA, Spain and Sweden.

Research and development continued throughout World War II to develop new and more powerful explosives and explosive compositions. Torpex (TNT/RDX/aluminium) and cyclotetramethylenetetranitramine, known as Octogen [(HMX) (C<sub>4</sub>H<sub>8</sub>N<sub>8</sub>O<sub>8</sub>)], became available at the end of World War II. In 1952 an explosive composition called 'Octol' was developed; this contained 75% HMX and 25% TNT. Mouldable plastic explosives were also developed during World War II; these often contained vaseline or gelatinized liquid nitro compounds to give a plastic-like consistency. A summary of explosive compositions used in World War II is presented in Table 1.1.

**Table 1.1** Examples of explosive compositions used in World War II.

Name	Composition
Baronal	Barium nitrate, TNT and aluminium
Composition A	88.3% RDX and 11.7% non-explosive plasticizer
Composition B (cyclotol)	RDX, TNT and wax
H-6	45% RDX, 30% TNT, 20% aluminium and 5% wax
Minol-2	40% TNT, 40% ammonium nitrate and 20% aluminium
Pentolites	50% PETN and 50% TNT
Picratol	52% Picric acid and 48% TNT
PIPE	81% PETN and 19% Gulf Crown E Oil
PTX-1	30% RDX, 50% tetryl and 20% TNT
PTX-2	41–44% RDX, 26–28% PETN and 28–33% TNT
PVA-4	90% RDX, 8% PVA and 2% dibutyl phthalate
RIPE	85% RDX and 15% Gulf Crown E Oil
Tetrytols	70% Tetryl and 30% TNT
Torpex	42% RDX, 40% TNT and 18% aluminium

### 1.6.7 Polymer Bonded Explosives

Polymer bonded explosives (PBXs) were developed to reduce the sensitivity of the newly-synthesized explosive crystals by embedding the explosive crystals in a rubber-like polymeric matrix. The first PBX composition was developed at the Los Alamos Scientific Laboratories in USA in 1952. The composition consisted of RDX crystals embedded in plasticized polystyrene. Since 1952, Lawrence Livermore Laboratories, the US Navy and many other organizations have developed a series of PBX formulations, some of which are listed in Table 1.2.

HMX-based PBXs were developed for projectiles and lunar seismic experiments during the 1960s and early 1970s using Teflon (polytetrafluoroethylene) as the binder. PBXs based on RDX and RDX/PETN have also been developed and are known as Semtex. Development is continuing in this area to produce PBXs which contain polymers that are energetic and will contribute to the explosive performance of the PBX. Inert prepolymers have been substituted by energetic prepolymers [mainly hydroxy terminated polybutadiene (HTPB)] in explosive compositions, in order to increase the explosive performance, without compromising its vulnerability to accidental initiation. In the last ten years it has become apparent that PBXs containing inert or energetic binders are more sensitive to impact compared to traditional explosive compositions. The addition of a plasticizer has reduced the sensitivity of PBXs whilst improving its processability and mechanical properties. Energetic plasticizers have also been developed for PBXs. Examples of energetic polymers and energetic plasticizers under investigation are presented in Tables 1.3 and 1.4, respectively.

**Table 1.2** Examples of PBX compositions, where HMX is cyclotramethylene-tetranitramine (Octogen), HNS is hexanitrostilbene, PETN is pentaerythritol tetranitrate, RDX is cyclotrimethylenetrinitramine (Hexogen) and TATB is 1,3,5-triamino-2,4,6-trinitrobenzene.

Explosive	Binder and plasticizer
HMX	Acetyl-formyl-2,2-dinitropropanol (DNPAF) and polyurethane
HMX	Cariflex (thermoplastic elastomer)
HMX	Hydroxy-terminated polybutadiene (polyurethane)
HMX	Hydroxy-terminated polyester
HMX	Kraton (block copolymer of styrene and ethylene-butylene)
HMX	Nylon (polyamide)
HMX	Polyester resin-styrene
HMX	Polyethylene
HMX	Polyurethane
HMX	Poly(vinyl) alcohol
HMX	Poly(vinyl) butyral resin
HMX	Teflon (polytetrafluoroethylene)
HMX	Viton (fluoroelastomer)
HNS	Teflon (polytetrafluoroethylene)
NTO	Cariflex (block copolymer of butadiene-styrene)
NTO/HMX	Cariflex (block copolymer of butadiene-styrene)
NTO/HMX	Estane (polyester polyurethane copolymer)
NTO/HMX	Hyttemp (thermoplastic elastomer)
PETN	Butyl rubber with acetyl tributylcitrate
PETN	Epoxy resin-diethylenetriamine
PETN	Kraton (block copolymer of styrene and ethylene-butylene)
PETN	Latex with bis-(2-ethylhexyl adipate)
PETN	Nylon (polyamide)
PETN	Polyester and styrene copolymer
PETN	Poly(ethyl acrylate) with dibutyl phthalate
PETN	Silicone rubber
PETN	Viton (fluoroelastomer)
PETN	Teflon (polytetrafluoroethylene)
RDX	Epoxy ether
RDX	Exon (polychlorotrifluoroethylene/vinylidene chloride)
RDX	Hydroxy-terminated polybutadiene (polyurethane)
RDX	Kel-F (polychlorotrifluoroethylene)
RDX	Nylon (polyamide)
RDX	Nylon and aluminium
RDX	Nitro-fluoroalkyl epoxides
RDX	Polyacrylate and paraffin
RDX	Polyamide resin
RDX	Polyisobutylene/Teflon (polytetrafluoroethylene)
RDX	Polyester
RDX	Polystyrene
RDX	Teflon (polytetrafluoroethylene)
TATB/HMX	Kraton (block copolymer of styrene and ethylene-butylene)

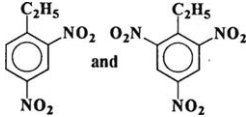
**Table 1.3** Examples of energetic polymers.

Common name	Chemical name	Structure
GLYN (monomer)	Glycidyl nitrate	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{C}-\text{CH}-\text{CH}_2\text{ONO}_2 \end{array}$
polyGLYN	Poly(glycidyl nitrate)	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\   \\ -[\text{CH}_2-\text{CH}-\text{O}]_n- \end{array}$
NIMMO (monomer)	3-Nitratomethyl-3-methyl oxetane	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_2\text{ONO}_2 \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \backslash \quad / \\ \text{O} \end{array}$
polyNIMMO	Poly(3-nitratomethyl-3-methyl oxetane)	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_2\text{ONO}_2 \\ \diagdown \quad / \\ -[\text{O}-\text{CH}_2-\text{C}-\text{CH}_2]_n- \end{array}$
GAP	Glycidyl azide polymer	$\begin{array}{c} \text{CH}_2\text{N}_3 \\   \\ -[\text{CH}_2-\text{CH}-\text{O}]_n- \end{array}$
AMMO (monomer)	3-Azidomethyl-3-methyl oxetane	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_2\text{N}_3 \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \backslash \quad / \\ \text{O} \end{array}$
PolyAMMO	Poly(3-azidomethyl-3-methyl oxetane)	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_2\text{N}_3 \\ \diagdown \quad / \\ -[\text{O}-\text{CH}_2-\text{C}-\text{CH}_2]_n- \end{array}$
BAMO (monomer)	3,3-Bis-azidomethyl oxetane	$\begin{array}{c} \text{N}_3\text{H}_2\text{C} \quad \text{CH}_2\text{N}_3 \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \backslash \quad / \\ \text{O} \end{array}$
PolyBAMO	Poly(3,3-bis-azidomethyl oxetane)	$\begin{array}{c} \text{N}_3\text{H}_2\text{C} \quad \text{CH}_2\text{N}_3 \\ \diagdown \quad / \\ -[\text{O}-\text{CH}_2-\text{C}-\text{CH}_2]_n- \end{array}$

## 1.7 Recent Developments

Recent developments in explosives have seen the production of hexanitrostilbene [(HNS) ( $\text{C}_{14}\text{H}_6\text{N}_6\text{O}_{12}$ )] in 1966 by Shipp, and triamino-trinitrobenzene {(TATB)  $[(\text{NH}_2)_3\text{C}_6(\text{NO}_2)_3]$ } in 1978 by Adkins and Norris. Both of these materials are able to withstand relatively high temperatures compared with other explosives. TATB was first prepared in 1888 by Jackson and Wing, who also determined its solubility characteristics. In the 1950s, the USA Naval Ordnance Laboratories recognized TATB as a useful heat-resistant explosive, and successful small-scale preparations and synthetic routes for large-scale production were achieved to give high yields.

**Table 1.4** Examples of energetic plasticizers.

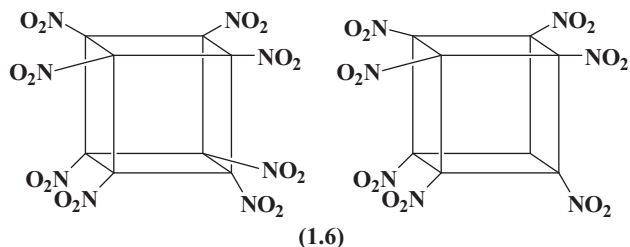
Common name	Chemical name	Structure
NENAs	Alkyl nitrateethyl nitramines	$\text{R}-\overset{\text{NO}_2}{\text{N}}-\text{CH}_2-\text{CH}_2\text{ONO}_2$
EGDN	Ethylene glycol dinitrate	$\text{O}_2\text{NOH}_2\text{C}-\text{CH}_2\text{ONO}_2$
MTN	Metriol trinitrate	$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{ONO}_2 \\   \\ \text{CH}_2\text{ONO}_2 \end{array}$
BTTN	Butane-1,2,4-triol trinitrate	$\begin{array}{c} \text{ONO}_2 \\   \\ \text{O}_2\text{NOH}_2\text{C}-\text{CH}-\text{CH}_2-\text{CH}_2\text{ONO}_2 \end{array}$
K10	Mixture of di- and tri-nitroethylbenzene	
BDNPA/BDNFA	Mixture of bis-dinitropropylacetal and bis-dinitropropylformal	$\begin{array}{c} \text{O}_2\text{N}-\text{C}(\text{NO}_2)-\text{O}-\text{C}(\text{NO}_2)-\text{O}-\text{C}(\text{NO}_2)-\text{CH}_3 \\   \quad   \quad   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ and $\begin{array}{c} \text{O}_2\text{N}-\text{C}(\text{NO}_2)-\text{O}-\text{C}(\text{NO}_2)-\text{O}-\text{C}(\text{NO}_2)-\text{CH}_3 \\   \quad   \quad   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$

Nitro-1,2,4-triazole-3-one [(NTO)(C<sub>2</sub>H<sub>2</sub>N<sub>4</sub>O<sub>3</sub>)] is one of the new explosives with high energy and low sensitivity. It has a high heat of reaction and shows autocatalytic behaviour during thermal decomposition. NTO was first reported in 1905 from the nitration of 1,2,4-triazol-3-one. There was renewed interest in NTO in the late 1960s, but it wasn't until 1987 that Lee, Chapman and Coburn reported the explosive properties of NTO. NTO is now widely used in explosive formulations, PBXs, and gas generators for automobile inflatable airbag systems. The salt derivatives of NTO are also insensitive and are potential energetic ballistic additives for solid rocket propellants.

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (C<sub>6</sub>H<sub>6</sub>N<sub>12</sub>O<sub>12</sub>) or HNIW, more commonly called CL-20 belongs to the family of high energy dense caged nitramines. CL-20 was first synthesized in 1987 by Arnie Nielsen, and is now being produced at SNPE in France in quantities of 50–100 kg on an industrial pilot scale plant.

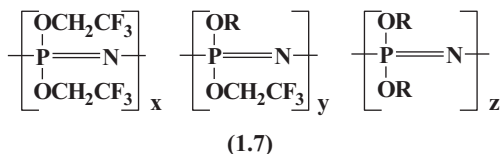
Nitrocubanes are probably the most powerful explosives with a predicted detonation velocity of >10 000 m s<sup>-1</sup>. Cubanes were first synthesized at the University of Chicago, USA by Eaton and Cole in 1964. The US Army Armament Research Development Center (ARDEC) then funded development into the formation of octanitrocubane [(ONC) (C<sub>8</sub>N<sub>8</sub>O<sub>16</sub>)] and heptanitrocubane [(HpNC) (C<sub>8</sub>N<sub>7</sub>O<sub>14</sub>)]. ONC and HpNC 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 (1.6). HpNC is denser than ONC and predicted to be a more powerful, shock-insensitive explosive.



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 hydrazinium nitroformate (HNF) and ammonium dinitramide (ADN). The majority of the development of HNF has been carried out in The Netherlands whereas the development of ADN has taken place in Russia, USA and Sweden. ADN is a dense non-chlorine 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.

Recent developments in polymeric binders are in the new family of polyphosphazenes. These polymers are highly flexible with very low glass transition temperatures and have a wide range of structures and physical properties.



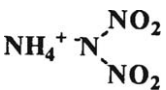
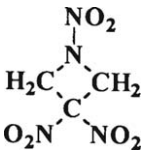
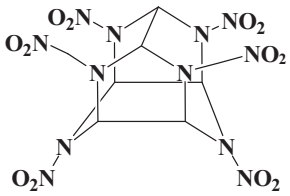
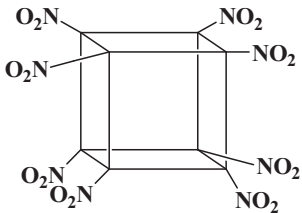
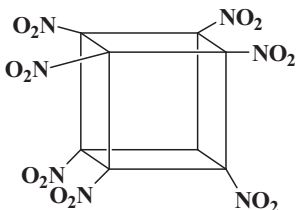
Polyphosphazenes (1.7) are polymers containing nitrogen as part of their backbone; they are commonly used in O-rings, pipelines, seals in the oil industry, fuel delivery, and storage systems. Polyphosphazene derivatives are biocompatible, biodegradable, and bioactive, and some of them are being investigated for possible medical applications. In 1995 attempts were made to synthesis energetic polyphosphazenes by Colclough and in 2006 Golding and Trussel patented the synthesis of energetic polyphosphazenes. Their materials possessed high energy density and lower glass transition



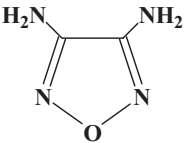
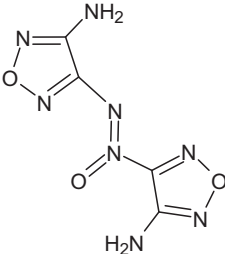
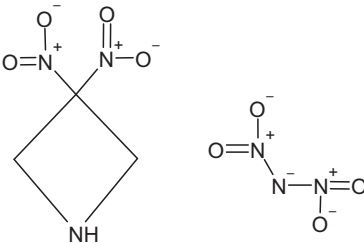
temperatures than existing materials such as GAP, polyNIMMO and polyGLYN, and could undergo chemical modification to produce a tacky and rubbery polymer which could be used as a binder in PBXs.

Examples of some explosive molecules under development are presented in Table 1.5. A summary of the significant discoveries in the history of explosives throughout the world is presented in Table 1.6.

**Table 1.5** Examples of explosive molecules under development.

Common name	Chemical name	Structure
ADN	Ammonium dinitramide	
TNAZ	1,3,3-Trinitroazetidine	
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	
HNF	Hydrazinium nitroformate	$\text{H}_2\text{N}-\text{NH}_3\text{C}(\text{NO}_2)_3$
ONC	Octanitrocubane	
HpNC	Heptanitrocubane	

**Table 1.5** (Continued)

Common name	Chemical name	Structure
DAF	3,4-Diaminofurazan	
DAAF	3,3'-Diamino-4,4'-azoxyfurazan	
DNAZ-DN	Dinitroazetidinium dinitramide	

## 1.7.1 Co-crystallization

The energetic community is still seeking to manufacture new explosives and propellants with improved performance and enhanced insensitivity to thermal or mechanical shock. The area of co-crystallization is currently being investigated to see if this is a viable technique.

Co-crystallization is used to improve the physical and chemical properties of a crystalline solid. It has been widely used in the field of pharmaceuticals where the rate of dissolution, thermal stability and biological activity of a drug can be improved without changing the structure of the active ingredient. This technology is currently being applied to energetic materials as an effective means of changing the density, melting point, decomposition temperature and sensitivity of explosives.

Landenberger and Matzger have produced 17 TNT co-crystals. When compared to TNT the co-crystals have different properties, such

**Table 1.6** Some significant discoveries in the history of incendiaries, fireworks, blackpowder and explosives.

Date	Explosive
220 BC	Chinese alchemists accidentally made blackpowder.
222–235 AD	Alexander VI of the Roman Empire called a ball of quicklime and asphalt 'automatic fire' which spontaneously ignited on coming into contact with water.
690	Arabs used blackpowder at the siege of Mecca.
940	The Chinese invented the 'Fire Ball' which is made of an explosive composition similar to blackpowder.
1040	The Chinese built a blackpowder plant in Pein King.
1169–1189	The Chinese started to make fireworks.
1249	Roger Bacon first made blackpowder in England.
1320	The German, Schwartz studied blackpowder and helped it to be introduced into central Europe.
1425	Corning, or granulating, process was developed.
1627	The Hungarian, Kaspar Weindl used blackpowder in blasting.
1646	Swedish Bofors Industries began to manufacture blackpowder.
1654	Preparation of ammonium nitrate was undertaken by Glauber.
1690	The German, Kunkel prepared mercury fulminate.
1742	Glauber prepared picric acid.
1830	Welter explored the use of picric acid in explosives.
1838	The Frenchman, Pelouze carried out nitration of paper and cotton.
1846	Schönbein and Böttger nitrated cellulose to produce guncotton.
1846	The Italian, Sobrero discovered liquid nitroglycerine.
1849	Reise and Millon reported that a mixture of charcoal and ammonium nitrate exploded on heating.
1863	The Swedish inventor, Nobel manufactured nitroglycerine.
1863	The German, Wilbrand prepared TNT.
1864	Schultze prepared nitrocellulose propellants.
1864	Nitrocellulose propellants were also prepared by Vieile.
1864	Nobel developed the mercury fulminate detonator.
1865	An increase in the stability of nitrocellulose was achieved by Abel.
1867	Nobel invented Dynamite.
1867	The Swedish chemists, Ohlsson and Norrbin added ammonium nitrate to dynamites.
1868	Brown discovered that dry, compressed guncotton could be detonated.
1868	Brown also found that wet, compressed nitrocellulose could be exploded by a small quantity of dry nitrocellulose.
1871	Abel proposed that ammonium picrate could be used as an explosive.
1873	Sprengel showed that picric acid could be detonated.
1875	Nobel mixed nitroglycerine with nitrocellulose to form a gel.
1877	Mertens first prepared tetryl.
1879	Nobel manufactured Ammonium Nitrate Gelatine Dynamite.
1880	The German, Hepp prepared pure 2,4,6-trinitrotoluene (TNT).
1883	The structure of tetryl was established by Romburgh.
1883	The structure of TNT was established by Claus and Becker.
1885	Turpin replaced blackpowder with picric acid.
1888	Jackson and Wing first prepared TATB.
1888	Picric acid was used in British Munitions called Liddite.
1888	Nobel invented Ballistite.
1889	The British scientists, Abel and Dewar patented Cordite.
1891	Manufacture of TNT began in Germany.

**Table 1.6** (Continued)

Date	Explosive
1894	The Russian, Panpushko prepared picric acid.
1894	Preparation of PETN was carried out in Germany.
1899	Preparation of RDX for medicinal use was achieved by Henning.
1899	Aluminium was mixed with TNT in Germany.
1900	Preparation of nitroguanidine was developed by Jousselein.
1902	The German Army replaced picric acid with TNT.
1905	NTO was first reported from the nitration of 1,2,4-triazol-3-one.
1906	Tetryl was used as an explosive.
1912	The US Army started to use TNT in munitions.
1920	Preparation of RDX by the German, Herz.
1925	Preparation of a large quantity of RDX in the USA.
1940	Meissner developed the continuous method for the manufacture of RDX.
1940	Bachmann developed the manufacturing process for RDX.
1943	Bachmann prepared HMX.
1946	HNF first synthesized by Hunter and reported in the British Intelligence Objectives Sub Committee.
1952	PBXs were first prepared containing RDX, polystyrene and dioctyl phthalate in the USA.
1952	Octols were formulated.
1957	Slurry explosives were developed by the American, Cook.
1964	Cubanes were first synthesized at the University of Chicago, USA by Eaton and Cole.
1966	HNS was prepared by Shipp.
1970	The USA companies, Ireco and Dupont produced a gel explosive by adding paint-grade aluminium and MAN to ANFO.
1978	Adkins and Norris prepared TATB.
1981	DAAF was first synthesized by Russian scientists Solodyuk, Boldyrev, Gidaspov and Nikolaev.
1983	TNAZ was first prepared at Fluorochem Inc.
1987	Lee, Chapman and Coburn reported the explosive properties of NTO.
1987	CL20 was first synthesized by Arnie Nielsen.
1997	ONC was successfully synthesized by Eaton and coworkers.
1998	FOX-7 or 1,1-diamino-2,2-dinitroethene (DADNE) was first synthesized by the Swedish National Defence Research Institute (FOA).
2000	HpNC was successfully synthesized by Eaton and coworkers.
2020	BDAFM or bis(3,4-diaminofurazan)methane was synthesized in China by Dong, Wang, Zhang, Li and Xu.

as density, melting point and decomposition temperature. Co-crystals of HMX have also been reported which result in a reduction in sensitivity compared to pure HMX. In order to improve the safety properties of CL-20, co-crystals of CL-20 and HMX were produced which were found to have similar safety properties to HMX with performance properties similar to CL-20. However, co-crystallization of these materials is not easy to obtain and more work is being conducted in this area.

### 1.7.2 Nano Explosives

It has been demonstrated by modelling that initiation and combustion of explosives are strongly influenced by their microscopic properties. Therefore, reducing the particle size to the nanoscale should result in a reduction of the mass-transport rate and therefore an increase in the burning rate. The modellers have also shown that nano explosives have higher energy densities, faster rate of energy release, and greater stability. However, the experimentalists have found that it is difficult to get a homogeneous mix of nano metal particles with propellants which results in compositions which do not have an increase in reaction temperature and burn rate. They have found that combustion is not reproducible particularly for ammonium perchlorate-based propellants. Nano ammonium nitrate/RDX powders have been synthesized by vacuum condensation of the evaporated bulk substrate onto a cooled substrate to obtain the nano powders. The resultant nano powder (particle size of 50 nm) has a faster burn rate of  $30 \text{ mm s}^{-1}$  when compared to RDX ( $15.1 \text{ mm s}^{-1}$ ) with a particle size between 200 and  $50 \mu\text{m}$ .

Nano thermites have been more successful with a reproducible decrease in ignition time from 6 s to 20 ms for nano Al-MoO<sub>3</sub> compositions with an aluminium particle size of 50 nm. Results have shown that the initiation temperature, reaction properties and rate of propagation of the thermites are strongly influenced by the microscopic properties of the energetic material including the size of the components and the intimacy of contact.

Nano explosives are less well studied and there is contradictory evidence that the addition of nano aluminium to ammonium dinitramide (ADN) shows improvements in the velocity of detonation. However, other researchers have found results which contradict this.

### 1.7.3 Insensitive Munitions and Insensitive High Explosives

In an effort to improve munitions survivability and safety, several countries established a policy requiring all new munitions be capable of withstanding accidents, fires, or enemy attack. One method of addressing this requirement was the use of 'Insensitive Munitions' (IM). An IM is one that will not detonate under any condition other than its intended use. If it is struck by fragments from an explosion or hit by a bullet, it will not detonate. It also will not detonate if it is in close proximity to a target that is hit. In extreme temperatures, the IM will only burn. This increased safety allows greater numbers of munitions to be packaged, handled, stored and transported in smaller containers.

Three approaches are taken when designing IMs: firstly, the high energy device can be protected and transported with an external protection of some kind. Some munition shipping containers are designed to provide a degree of protection and thermal insulation. Secondly, the casings of high energy devices can be designed in such a way as to allow venting or some other form of pressure relief in a fire. Lastly, the chemistry of the high energy fill is chosen to provide a higher degree of stability, for example by using insensitive high explosives (IHE).

The IHE must be powerful enough to do the job and at the same time insensitive enough to prevent accidental explosion, for example CL-20 has an energy density at least 15% greater than that of HMX but it is not an IHE due to its sensitivity to impact, whereas LLM-105 [2,6-pyrazinediamine, 3,5-dinitro-1-oxide ( $C_4H_4N_6O_5$ )] has 60% more energy than TNT and is classed as an IHE. TATB is a reasonably powerful high explosive which has a thermal and shock stability that is considerably greater than that of any other known material of comparable energy and is, therefore, a good candidate for IHE. In the late 1990s Groupe SNPE, (France's state-owned producer of space and military propellants and explosives) produced a reduced sensitivity form of RDX (RS-RDX) for use in IHE formulations. Other manufacturers soon produced forms of RS-RDX such as I RDX (Insensitive RDX) and Grade A RDX. A version of RS-HMX has also been manufactured in Norway by Chemring Nobel AS. Examples of IHE formulations are presented in Table 1.7.

### 1.7.4 High Energy Density Materials (HEDMs)

Another area of development is the high density, high performing, insensitive explosives which are known as high energy density materials (HEDMs) or high energy materials (HEMs). HEDMs are based on nitrogen-rich compounds such as furazans, tetrazoles and pyrazoles because they have high enthalpies of formation, good detonation properties and the gaseous products are less toxic to the environment.

## 1.8 Explosives and the Environment

Up until the mid-1980s, surplus and unserviceable energetic materials, munitions and propellants were either dumped at sea or destroyed by open burning and open detonation. Sea dumping, open burning and open detonation were the preferred disposal techniques because of their simplicity, low cost, effectiveness and safety. However, concern

**Table 1.7** Examples of insensitive high explosives (IHE) formulations where CAB is cellulose acetate butyrate, DNAN is 2,4-dinitroanisole, HTPB is hydroxyterminated polybutadiene, IPDI is isophorone diisocyanate and Kel F 800 is chlorotri-fluoroethylene-co-vinylidene fluoride polymer.

Name	Explosive\%wt	Binder + plasticizer\%wt	Other ingredients\%wt
LX-17	92.5 TATB	7.5 Kel-F 800	
PAX-2A(1)	85 HMX	1.6 CAB 9 K10	N/A Carbon
PAX-21	36 RDX		30 Ammonium perchlorate
	34 DNAN		<i>n</i> -methyl nitroaniline
PAX-24	N/A DNAN		Ammonium perchlorate
			<i>n</i> -methyl nitroaniline
PAX-25	N/A RDX		Ammonium perchlorate
	N/A DNAN		<i>n</i> -methyl nitroaniline
PAX-26	N/A DNAN		Aluminium Ammonium perchlorate
			<i>n</i> -methyl nitroaniline
PAX-28	20 RDX		20 Aluminium
	40 DNAN		20 Ammonium perchlorate
			<i>n</i> -methyl nitroaniline
PAX-40	65 HMX 35 DNAN		<i>n</i> -methyl nitroaniline
PAX-41	65 RDX 35 DNAN		Nitroaniline
PBXW-124	27 NTO	5 HTPB	20 Aluminium
	20 RDX	7 IPDI	20 Ammonium perchlorate
PBXW-122	47 NTO	5 HTPB	15 Aluminium
	5 RDX	7 IPDI	20 Ammonium perchlorate

has grown in recent years over the protection of human health and the environment and it is generally accepted that sea dumping, open burning and open detonation activities have the potential to cause harm. As a result, sea dumping is now banned while open burning and open detonation operations are becoming increasingly restricted. Countries such as Germany and the Netherlands prohibit open burning and open detonation activities and others restrict it, for example in the US and Canada. There is a concern however, that activities in the past have led to contamination of the land, soil and water.

There are various explosive related activities that can contribute to contaminating land, soil and water these include manufacturing plants, firing ranges, open burning, open detonation and munitions which have been left in the ground from previous conflicts, *i.e.*, World War I and II. For example, in 1914–1918 in the UK, waste containing picric acid from the manufacture of explosives were placed in abandoned chalk pits and in the early 1920s water from a nearby well was reported to have a yellow tint. By 1942 the pollutant had migrated at least a mile as indicated by another contaminated well. From 1939

until 1955 water samples around the area were reported to have this characteristic yellow picric acid tint. Studies have been conducted on the effect TNT, RDX, HMX and other explosives have on the environment. TNT has been found to be soluble in water and has a tendency to degrade by photolysis, whereas RDX and HMX are less soluble in water and therefore leach out of the soil to groundwater (see Table 1.8). In order to reduce, control and monitor explosive

**Table 1.8** Explosives properties that can affect the environment.

Explosive	Environmental properties <sup>a</sup>	Environmental consequences <sup>a</sup>
TNT	Fast dissolution rate, adsorbs strongly to soil but also degrades readily. Depending on soil characteristics, these breakdown products are either more mobile than, or have a similar mobility to, TNT. TNT can be taken up by plants from contaminated soil, including edible varieties of garden plants, aquatic and wetland plants, trees, and can accumulate in plant roots.	Lethal concentration of TNT to plants in water is $5000 \mu\text{g L}^{-1}$ . Phytotoxicity from contaminated soil is dependant on soil properties, for example, plant yields are significantly reduced in silty soils when TNT concentrations reach $200 \text{ mg kg}^{-1}$ but no effects are observed at concentrations of less than $400 \text{ mg kg}^{-1}$ in clay. Laboratory research has also shown that TNT concentrations in soil greater than $9000 \text{ mg kg}^{-1}$ result in no surviving earthworms, whilst male animals treated with high doses of TNT have developed serious reproductive system effects.
RDX	Dissolves very slowly in water, does not adsorb strongly to soil and migrates further in contaminant plumes in ground-water. It is not bioaccumulative in plant or animal tissues but can be taken up by plants from contaminated soils, thus small amounts could be transferred up the food chain	Plant species have been found to die in RDX contaminated soils at concentrations of $580 \text{ mg kg}^{-1}$ . Studies into the phytotoxicity of RDX indicate a lethal concentration in water of $5$ to $6 \text{ mg L}^{-1}$ with stunted growth of emergent species experienced at concentrations of $1.5 \text{ mg L}^{-1}$ .
HMX	Adsorbs to soil to a lesser degree than TNT, is more soluble than RDX and is resistant to biodegradation in aquifers. Degradation and its breakdown products have rarely been found in the environment.	Potential to cause liver and central nervous system damage but it is not known whether it causes cancer or reproductive problems in animals.

<sup>a</sup>Some of this information is taken from Warde, C, Lee, R and Baker, A, 2007.



waste, environmental legislations have been implemented. These legislations include the Water Resources Act, Groundwater Regulation and Environmental Protection Act (see Table 1.9).

**Table 1.9** Environmental legislations which have an impact on explosive waste.

Environmental legislation	Comment
Environmental Protection Act 1990	This defines the term contaminated land, where there is a release of substances that can cause harm.
Clean Air Act 1993	It is an offence to cause dark smoke to be emitted from a facility. Dark smoke is defined as smoke that is as dark as, or darker than, shade 2 on the Ringelmann Chart (BS 2742C:1957).
Water Resources Act 1991 and Water Act 2003	It is an offence to cause or knowingly permit poisonous, noxious or polluting matter, or any solid waste matter, to enter controlled waters (which include groundwater).
Groundwater Regulations 1998	A list of materials that must be either prevented from reaching groundwater (red list) or whose introduction to groundwater should be reduced (grey list). Explosive compounds are not included on these lists but certain metals such as lead, copper, zinc and cadmium are.
Water Framework Directive 2000	Protection of inland surface waters, transitional waters, coastal waters and groundwater.
Waste Incineration Directive 2000	This prevents the release of toxic substances to the atmosphere.
Environmental Liability Directive 2004	Establishes a framework to prevent and remedy environmental damage.
Contaminated Land (England) Regulations 2006	The regulations on contaminated land are designed to prevent new land becoming contaminated by polluting substances whilst also tackling historic contamination of sites.
The REACH Enforcement Regulations 2008	Provides a high level of protection of human health and the environment from the use of chemicals and to promote the use of alternative methods for the assessment of the hazardous properties of substances.
Environmental Permitting Regulations 2010	All emitting activities from regulated facilities have the appropriate permits as awarded by the Environment Agency.
Draft Waste and Environmental Permitting <i>etc.</i> (Legislative Functions and Amendment <i>etc.</i> ) (EU Exit) Regulations 2020	Ensures that the waste and environmental permitting regimes continue to operate effectively at the end of the Brexit transition period.
Environment Bill 2020	Plan to protect and improve the natural environment in the UK which includes the management and prevention of waste including air and water pollution and REACH.

**Table 1.10** Examples of processes for the recovery of explosives from the casing.

Removal of explosive from casing	Explosive	Status
Melt-out and filtration	TNT, TNT/RDX	Current Practice
Cryogenic wash-out	TNT, TNT/RDX, PBX	Current Practice
High pressure water jet	TNT, TNT/RDX, HMX, RDX, PBX	Current Practice
Induction heating	TNT, TNT/RDX	Current Practice
Microwave melt-out	TNT, TNT/RDX	Development
Ammonia wash-out	TNT, TNT/RDX	Development
Supercritical solvent extraction	TNT, TNT/RDX, RDX, HMX, PBX	Research

With regards to the future, explosives may be made ‘greener’ by using smaller amounts of toxic reagents and solvents, and having a reduced environmental impact. The term ‘green chemistry’ was first used by Anastas and Warner in 1998 where toxic or noxious reagents are replaced with more environmentally acceptable ones, whilst minimizing waste and energy and maximizing product yield. One way of making explosives greener is to reduce its environmental impact by recycling the explosives. This has been achieved with TNT where TNT based compositions are melted using a hot water bath. The recovered TNT is then solidified and re-used. However, with the new IHE compositions containing PBXs this method is not viable. Methods are, therefore, being developed to remove the waste explosive compositions safely from the casing using mechanical methods or high-pressure water jets. The recovered material then has to be disposed of or recycled. Table 1.10 lists details of current and future technologies for the recovery of explosives.

Another area where the energetic community is making changes is the introduction of new ‘cleaner’ chemicals. Here environmentally friendly solvents replace the toxic solvents. Ionic liquids, supercritical fluids and neoteric solvents have been investigated as suitable alternatives.

Ionic liquids which include salts, have a melting point below 100 °C and they are in the liquid state to a temperature of about 400 °C. Ionic liquids have been found to significantly improve the selectivity of nitration of aromatic compounds.

### 1.8.1 Environmental Legislation

Both the manufacturers and users of explosives are responsible for any adverse impact on the environment from the explosives.

Examples of relevant environmental legislation are (i) Contaminated Land (England) Regulations 2006, (ii) Water Resources Act 1991 and (iii) the Environmental Permitting Regulations 2010.

The Water Framework Directive (WFD) (2000/60/EC) sets out strategies against the pollution of water and mandates that all bodies of surface and groundwater need to achieve 'Good Status' and anyone discharging wastewaters must obtain a permit and must comply with the discharge limits, based on whether wastewaters are industrial, household or urban. This is also enforced under the Industrial Emissions Directive whereby all discharges to air, land and water from industrial installations, including those that produce explosives, require a permit and continual monitoring.

Environmental remediation of polluted sites is covered by the Legislative Decree 152/2006, where the responsibility for remediation is shared between the regions and the provinces. If the levels of contaminants exceed the maximum permitted concentrations after the waste has been removed, the area must be characterized and, if necessary, reclaimed. The Environmental Liability Directive 2004/35/EC establishes a framework regarding prevention and remediation of the environmental damage.

An area where not so much work has been done is the eco-toxicology threshold limits for energetics in soil and water. The United States Environmental Protection Agency (US EPA) has established guideline exposure limits for the most common energetic contaminants and their degradation products (EPA 2014a and 2014b), and these limits are frequently applied by other nations. There is also a section on nuisance in the Environmental Protection Act 1990, where noise from explosions, and odour and black smoke from open-burning for disposal are included.

The most recent and significant legislation is the UK Environment Bill 2020 which sets out a new environmental governance framework as the UK leaves the European Union's environmental policy and legislative structures. It covers waste and resources, air quality, water and nature and biodiversity. A summary of the recent Environmental Acts is presented in Table 1.9.