Introduction to Explosives

DEVELOPMENT OF BLACKPOWDER

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. They added potassium nitrate [also known as saltpetre (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 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. 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.

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. discovered Ascanio Sobrero liauid nitroglycerine $[C_2H_5O_3(NO_3)_2]$. 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 [Hg(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 into 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.

$$H$$
 $H-C-O-NO_2$
 $H-C-O-NO_2$
 H
 $H-C-O-NO_2$
 H

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 became 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.

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.

DEVELOPMENT OF DYNAMITE

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 (NH₄NO₃). Alfred Nobel subsequently acquired the patent of Ohlsson and Norrbin for ammonium nitrate and used this in his explosive compositions.

Development of Ammonium Nitrate

Ammonium nitrate was first prepared in 1654 by Glauber but it was not until the beginning of the 19th century when 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 is much more dangerous than previously thought and more rigid regulations governing its storage, loading and transporting in the USA were promptly put into effect.

DEVELOPMENT OF COMMERCIAL EXPLOSIVES

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.

Development of ANFO and Slurry 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

DEVELOPMENT OF MILITARY EXPLOSIVES

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.

$$O_2N \longrightarrow NO_2$$

$$NO_2$$

$$(1.2)$$

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 acci-

dental initiation, and picric acid required prolonged heating at high temperatures in order for it to melt.

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.

$$H_3C$$
 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2 NO_2

Development of TNT

Around 1902 the Germans and British had experimented with trinitrotoluene [(TNT) ($C_7H_5N_3O_6$)], first prepared by Wilbrand in 1863. The first detailed study of the preparation of 2,4,6-trinitrotoluene was by Beilstein and Kuhlberh 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.

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 (CH₄N₄O₂) 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) ($C_3H_6N_6O_6$)] also called Cyclonite or Hexogen, and pentaerythritol tetranitrate [(PETN) ($C_5H_8N_4O_{12}$)].

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.

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 Bridgewater. 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 cyclotetramethylenetetranit-ramine, known as Octogen [(HMX) ($C_4H_8N_8O_8$)], became available at the end of World War II. In 1952 an explosive composition called

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

Table 1.1 Examples of explosive compositions used in World War II

'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.

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 (polytetra-fluoroethylene) 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. Energetic plasticizers have also been developed for PBXs.

Table 1.2 Examples of PBX compositions, where HMX is cyclotetramethyleneteranitramine (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)	
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/vinylidine 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)	

Examples of energetic polymers and energetic plasticizers under investigation are presented in Tables 1.3 and 1.4, respectively.

 Table 1.3 Examples of energetic polymers

Common name	Chemical name	Structure
GLYN (monomer)	Glycidyl nitrate	O H ₂ C-CH-CH ₂ ONO ₂
polyGLYN	Poly(glycidyl nitrate)	CH_2ONO_2 $$
NIMMO (monomer)	3-Nitratomethyl-3-methyl oxetane	H ₃ C CH ₂ ONO ₂ H ₂ C CH ₂
polyNIMMO	Poly(3-nitratomethyl-3-methyl oxetane)	O' H_3C CH_2ONO_2 $ -$
GAP	Glycidyl azide polymer	$\begin{array}{c} CH_2N_3 \\ - CH_2 - CH - O - \frac{1}{n} \end{array}$
AMMO (monomer)	3-Azidomethyl-3-methyl oxetane	H ₃ C CH ₂ N ₃ CH ₂ C CH ₂
PolyAMMO	Poly(3-azidomethyl-3-methyloxetane)	$\begin{array}{c} O \\ H_3C \\ \hline -O-CH_2-C-CH_2-I_n \end{array}$
BAMO (monomer)	3,3-Bis-azidomethyl oxetane	N ₃ H ₂ C CH ₂ N ₃
PolyBAMO (monomer)	Poly(3,3-bis-azidomethyl oxetane)	H ₂ C CH ₂ O CH ₂ N ₃

Table 1.4 Examples of energetic plasticizers

Common name	Chemical name	Structure
NENAs	Alkyl nitratoethyl nitramines	NO ₂ R-N-CH ₂ -CH ₂ ONO ₂
EGDN	Ethylene glycol dinitrate	O ₂ NOH ₂ C-CH ₂ ONO ₂
MTN	Metriol trinitrate	CH2ONO2 $H3C-C-CH2ONO2$ $CH2ONO2$
BTTN	Butane-1,2,4-triol trinitrate	ONO ₂ O ₂ NOH ₂ C-CH-CH ₂ -CH ₂ ONO ₂
K10	Mixture of di- and tri-nitroethylbenzene	$\begin{array}{c c} C_2H_5 & C_2H_5 \\ \hline NO_2 & O_2N & NO_2 \\ \hline & and & NO_2 \\ \hline \end{array}$
BDNPA/F	Mixture of bis-dinitropropylacetal and bis-dinitropropylformal	O ₂ N NO ₂ O ₂ N NO ₂ O O C H ₃ C CH ₂ CH ₂ CH ₂ CH ₃ and O ₂ N NO ₂ O ₂ N NO ₂ C O C CH ₂ CH ₃ CH ₃ C H ₃ C CH ₂ C CH ₃

Heat-resistant Explosives

More recent developments in explosives have seen the production of hexanitrostilbene [(HNS) ($C_{14}H_6N_6O_{12}$)] in 1966 by Shipp, and triaminotrinitrobenzene {(TATB) [(NH₂)₃C₆(NO₂)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

		•
Common name	Chemical name	Structure
NTO	5-Nitro-1,2,4-triazol-3-one	O _C NH HN.N C-NO ₂
ADN	Ammonium dinitramide	$NH_4^+ N$ NO_2
TNAZ	1,3,3-Trinitroazetidine	$ \begin{array}{c} NO_2\\ N\\ C \end{array} $ $ \begin{array}{c} N\\ CH_2 \end{array} $ $ \begin{array}{c} O_2N \end{array} $ $ \begin{array}{c} N\\ O_2 \end{array} $
CL-20	2,4,6,8,10,12-Hexanitro- 2,4,6,8,10,12-hexa- azatetracyclododecane	O ₂ N CH NO ₂ O ₂ N CH NO ₂ CH CH NO ₂ NO ₂ NO ₂ NO ₂

 Table 1.5
 Examples of explosive molecules under development

small-scale preparations and synthetic routes for large-scale production were achieved to give high yields.

Research and development is continuing into explosive compounds which are insensitive to accidental initiation but still perform very well when suitably initiated. Examples of explosive molecules under development are presented in Table 1.5.

Finally, a summary of the significant discoveries in the history of explosives throughout the world is presented in Table 1.6.

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
1.405	be introduced into central Europe.
1425	Corning, or granulating, process was developed.
1627	The Hungarian, Kaspar Weindl used blackpowder in blasting.
1646 1654	Swedish Bofors Industries began to manufacture blackpowder 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
1050	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	110011
1867	Nobel invented Dynamite. The Swedish chemists, Ohlsson and Norrbin added
1007	ammonium nitrate to dynamites.
1868	Brown discovered that dry, compressed guncotton could be
1000	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
10.1	explosive.
1873	Sprengel showed that picric acid could be detonated.
1875	Nobel mixed nitroglycerine with nitrocellulose to form a gel.

Table 1.6 Continued

Date	Explosive	
1877	Mertens first prepared tetryl.	
1879	Nobel manufactured Ammoniun 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.	
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 Jousselin.	
1902	The German Army replaced picric acid with TNT.	
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	
15.0	manufacture of RDX.	
1940	Bachmann developed the manufacturing process for RDX.	
1943	Bachmann prepared HMX.	
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.	
1966	HNS was prepared by Shipp.	
1970	The USA companies, Ireco and Dupont produced a gel	
15.0	explosive by adding paint-grade aluminium and MAN to	
	ANFO.	
1978	Adkins and Norris prepared TATB.	