Chapter 14
Explosives

14.1 Introduction

The first recorded account of an explosive was the description of a crude form of gunpowder by Cheng Yin in China about 850 A.D. He cautioned about the dangers of burning the experimenter and the house. These warnings still apply today. The first European to refer to gunpowder was Roger Bacon who concealed the formula in a code which was not revealed for another century. By 1346, gunpowder (or black powder) was used to fire a cannon in battle. In the seventeenth century, it was used in mines as a blasting agent. This reaction is very practical at the present time and shown below:

$$4KNO_3 + 2S + 7C \rightarrow K_2CO_3 + K_2S_2 + 2N_2 + 3CO_2 + 3CO \qquad (14.1)$$

During the Napoleonic Wars, England produced over 20,000 barrels of gunpowder a year with each barrel weighing 100 lb. The modern era of explosives began in 1846 when Sobrero discovered nitroglycerin.

An explosive substance is one which undergoes a very rapid chemical reaction that is highly exothermic and which is accompanied by high pressures at the reaction site and the evolution of a large quantity of gaseous products. When noise is also produced due to a shock wave, the process is called a *detonation*, and the substance is called a *high explosive*. The distinguishing characteristics of an explosive relative to fuels and propellants are given in Table 14.1, where it can be seen that the heat of reaction is not important. The most significant property of an explosive is its high rate of reaction, or the power generated, and the pressure produced. When the linear speed of reaction of a substance (the propagation of the flame front) is in the range of meters/sec, the substance is classed as a low explosive and the process is called a *deflagration*.

Explosives are further divided into primary and secondary explosives. Primary explosives are detonated by heat, spark, flame, or mechanical impact, whereas secondary explosives can only be detonated by an externally applied shock wave such as commonly produced by a primary explosive.

Secondary explosives when ignited by a flame will normally burn without detonating. However, even low explosives can be made to detonate under suitable conditions depending on the material.

14.2 Primary Explosives

Some selected *primary explosives* and their properties are given in Table 14.2. Most of these initiators are toxic as well as unstable. They are usually combined with other initiators or other substances such as $KClO_3$, KNO_3, $Ba(NO_3)_2$, PbO_2, and Sb_2S_3.

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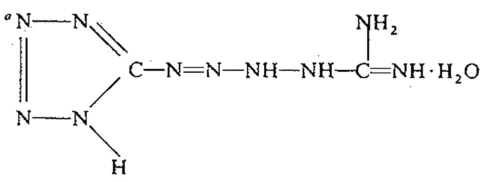
Table 14.1 The distinguishing characteristics of burning fuel, propellants, and explosives

Property	Burning fuel	Propellant	Explosive
Typical material	Coal, oil, gas	Hydrazine	TNT
Linear reaction	10^{-6}	10^{-2}	10^{3}
$t^{1/2}$ (s)	10^{-1}	10^{-3}	10^{-6}
Factors controlling reaction rate	Heat transfer	Heat transfer	Shock transfer
Energy output (J/g)	10^{4}	10^{3}	10^{3}
Power output (W/cm^2)	10	10^{3}	10^{9}
Common initiation mode	Heat	Hot gases and particulate	High temperature and high pressure shock waves
Pressure developed (atm)	1–10	10–1,000	10^{4}–10^{6}

Table 14.2 Some primary explosives and their properties

	Mercury fulminate	Lead azide	Silver azide	Lead styphnate	Tetrazene[a]	Diazodinitro-phenol
Formula	$Hg(ONC)_2$	$Pb(N_3)_2$	AgN_3	$C_5HN_3O_8Pb$	$C_2H_8N_{10}O$	$C_6H_2N_4O_5$
Formula wt (g/mol)	285	291	150	468	188	210
Density (g/mL)	4.43	4.71	5.1	3.08	1.7	1.63
Color	Grey	White	White	Tan	Yellow	Yellow
Melting point (°C)	100 exp.	Dec.	252	206 explodes	Dec.	150 ± 10 exp.
Ignition temp. (°C)	215	330	300	280	130	170
Minimum value for igniting TNT (mg)	360	90	70			
Heat of formation (kJ/g)	−0.941	−1.48	−2.07	1.83	1.13	−1.59
Heat of explosion (kJ/g) to $(H_2O)g$	1.78	1.53	1.90	1.91	2.75	3.43
Specific gas volume ml (STP)/g	316	310		368	1190	865
Activation energy (kJ/g)	30	170	150	260		230
Detonation (mm/μsec)	4.5	4.5	6.8	5.0		6.9
Velocity (km/s) at density (g/mL)	3.3	3.8	5.1	2.7		1.6
Sensitivity to impact (kgm)	0.18	0.41		0.15	5	16
Sensitivity to friction (kgf)	0.43	0.12		0.08		
Drop hammer, 2 kg height (cm)	4	10		35		
Sensitivity to static electrical energy max. for non-ignition (J)	0.07	0.01	0.007	0.001	0.036	0.25

[a]



The azides are usually unstable and are formed by the reaction of hydrazoic acid (HN_3) with the metal oxide. Sodium azide (NaN_3) is used to explosively fill air bags in car crashes. Silver azide (AgN_3) is more expensive than the lead azide, $Pb(N_3)_2$, which is the common detonator. Care must be taken during its production since large crystals readily explode. Contact with copper must be avoided since copper azide (CuN_3) is extremely sensitive. The high thermal stability of $Pb(N_3)_2$ makes it suitable for long-term storage.

The amounts of primary initiator needed to detonate a secondary explosive vary from 10 to 400 mg and depend on both components. The major requirements of a good initiator are that it must be sufficiently stable for safe manufacturing, compatible with metal casing, easily loaded into detonators, and not too expensive. Its storage under adverse conditions must not alter its properties or stability.

The initiators are sensitive to friction and shock (blow). The percussion sensitivity is measured by the drop-hammer method where a 2 kg steel ball is dropped from increasing heights until detonation occurs. The amount of electrical energy needed to initiate the detonation depends on the initiator.

Diazodinitrophenol, though sensitive to impact, is not as sensitive to friction or electrostatic energy but somewhat less stable to heat than lead azide.

Lead styphnate ($C_5HN_3O_8Pb$), or lead trinitroresorcinate, is very sensitive to electrostatic discharge and often used to sensitize lead azide.

Tetrazene ($C_2H_8N_{10}O$) is readily decomposed in boiling water and is usually used as an ignition agent for lead azide. It is very sensitive to percussion and friction.

Mercury fulminate ($Hg(CNO)_2$) was the first initiating explosive which has found extensive use. However, in comparison with other primary explosives, it is relatively weak and does not store well under adverse conditions and hence is not used much at present.

14.3 Secondary Explosives

The substances which have high detonation velocities but are relatively insensitive to shock can act as *secondary explosives*. Some common secondary explosions are listed in Table 14.3. There are about 120 different chemical compounds which have been used or can be used as explosives. Many are too unstable to be used industrially or for military applications. A practical explosive is one that is not too difficult to produce on a large scale; is stable when stored under various conditions of temperature, humidity, and vibrations; and is not too expensive.

Explosives are generally characterized by five features: (1) chemical stability, (2) sensitivity to ignition, (3) sensitivity to detonation, (4) velocity of detonation, and (5) explosive strength. These characteristics can have quantitative values with statistical variations which must meet stringent requirements, especially for military use. However, the occurrence of an unexpected explosion or dud may be statistically predictable when thousands or millions of events have been tried. Perfect reliability is something which can seldom be achieved.

14.3.1 Chemical Stability

The *chemical stability* of an explosive is determined by its ability to maintain its reactive characteristics and to remain chemically unchanged while stored or aged under specific conditions.

Thus, extreme temperatures of −30°C or +45°C often encountered during military operations can destabilize the materials of an explosive. Chemical instability may thus be due to the nonexplosive degradation or decomposition of the explosive substance with the result that the reliability and strength is decreased.

14.3.2 Sensitivity to Ignition

Explosive solids can be detonated by heat, mechanical impact, friction, or electrical spark or discharge. The sensitivity of an explosive is the effect of the stimulus on its spontaneous detonation:

Table 14.3 Properties of some selected secondary explosives of importance

Name	Composition	Density (g/mL)	Ignition (°C)	Det velocity (km/s)	Gap test related to TNT	ΔH^0 expl. (kJ/g)	Spec. gas vol. (mL(STP)/g)	Sensitivity to friction (kg f)	Height of drop hammer 2 kg/ (cm)	Comments
Black power (BP)	KNO_3, 15 C, 10 S	1.2	310	0.4		2.8	280		60	Cheap, smoky, sensitive
Nitrocellulose (NC)	Nitrated cotton	1.5	180	6.3		4.3	765	10–36	20	Smokeless, grain size controls rate
Nitroglycerin (NG)	$C_3H_5(ONO_2)_3$	1.6	200	7.8		6.2	715	0–36	4	Volatile, very high sensitivity
Blasting gelatin	92/8: NG/NC(BG)	1.5	190	7.5		6.4	712		12	Strongest high brisance
Gelatin/ dynamite	BG+Dope (20–90 %)[a]	1.5	190	6.3		5.3	600		17	Jelly; waterproof, powerful
Trinitrotoluene	TNT, $CH_3C_6H_2(NO_2)_3$	1.57	225	6.9	100	4.0	690	29.5	60	Easily melted, powerful
Tetryl	$C_7H_5N_5O_8$	1.7	195	7.2	50	4.6	710	27–36	40	Cast. waterproof
Amatol	50/50: NH_4NO_3+TNT1:1	1.5	220	6.5	45	4.0	815		55	Low sensitivity (like TNT) hygroscopic
	80/20: NH_4NO_3+TNT4:1	1.4	220	5.4	150	3.9	860		60	High thermal stability, 1.5 times stronger than TNT
Hexogen, RDX cyclonite	$C_3H_6N_6O_6$	1.6	260	7.5	40	4.3	910	1.5	20	Plastic easily molded (vaseline)
Plastic explosive	RDX+elastomer	1.65		8.0		5.0				

[a] Dope is oxygen balanced explosive of either $NaNO_3$, NH_4NO_3 or explosive oils such as ethylene glycol dinitrate

(a) The thermal stability is determined by immersing a 5-mg sample in a thin-walled metal container in a heated bath. The temperature, ranging from 100 to 300°C, at which the sample detonates after 5 s, is the ignition temperature. The thermal stability is also determined by increasing the temperature of the sample by 5°C/min until detonation occurs.

(b) Sensitivity to percussion and impact is illustrated by the percussion cap in ammunition, and the impact fuses in bombs and shells. The test involves a given mass of steel which is dropped from increasing heights onto a given mass of sample of particle size <1 mm and spread over a given area. The height from which the sample detonates 50% of the time is an indication of the hazards involved in handling the explosive.

(c) The frictional force (kgf) required to detonate the sample 50% of the time is determined by the sliding torpedo test or the pendulum scoring test. This value determines the ease of handling the material and precautions which must be taken.

(d) The sensitivity of an explosive to a spark or electric discharge is determined by the minimum energy required to detonate the sample. The electrostatic charge on clothing has often accidentally detonated explosives while being handled. Nonsparking tools (some made of beryllium-copper alloys) are normally used in factories where explosives are handled. The maximum static energy which will not detonate a secondary explosive is usually much higher than for a primary explosive.

14.3.3 Sensitivity to Detonation

The sensitivity to detonation of an explosive is determined by the ease with which the explosive can be ignited by the primary detonation or another explosive in the vicinity which generates a shock wave. A maximum gap between the initiated detonator and the test explosive determines the sensitivity of the explosive to detonation. This gap test is an important characteristic which is usually determined relative to trinitrotoluene (TNT).

14.3.4 Velocity of Detonation

The *velocity of detonation* (VOD) of an explosive is the rate at which the detonation wave passes through the explosive. The greater the VOD, the larger is the power of the explosive. The VOD is determined by several methods: an optical, an electrical, and a comparative method.

In the optical method, a high-speed streak camera is used to follow the flame front at about 10 million frames/s, with exposures of as little as 0.01 μs.

In the electrical method, a resistance element is embedded along the explosive axis, and as the detonation proceeds, the resistance changes and can be followed as a function of time on an oscilloscope.

A comparative method uses a standard detonating fuse with known VOD. A fixed known length of the standard fuse is placed in a parallel loop with the test explosive. The two ends of the standard fuse are in contact with the test explosive and when detonated will ignite both standard and test explosive. The larger path of the standard fuse means that the start and end parts both ignite, causing the two flame fronts to meet at a point which is identified by an indentation on a lead plate adjacent to the standard fuse. The VOD of the sample can be calculated from the distances and the VOD of the standard explosive (see Exercise 14.10).

14.3.5 Explosive Strength

The strength of an explosive is its most important characteristic and is a measure of the conversion of its exothermic energy of combustion into mechanical disruption or power. The strength is usually

Table 14.4 Properties of some common explosives

Explosive	Formula	Mol. wt. (g/mol)	Blasting strength	Oxygen balance (g/atom/kg)
Trinitrophenol	$C_6H_3N_3O_7$	229.1	106	−28.4
Trinitrotoluene	$C_7H_5N_2O_6$	227.1	100	−46.2
Tetryl	$C_7H_5N_5O_8$	287.2	126	−29.6
RDX (hexogen)	$C_3H_6N_6O_6$	222.1	150	−13.5
PETN	$C_3H_8N_4O_{12}$	316.2	146	−6.3
Nitroglycerin	$C_3H_5N_3O_9$	227.1	140	+2.2
Ammonium nitrate	NH_4NO_3	80.1		+12.5

determined on the basis of unit weight, but the more practical basis is in terms of unit volume. Weight strength of an explosive is readily determined by comparison with a standard explosive such as blasting gelatin which is classified at 100%. For comparison, dynamite with 40% nitroglycerin has a weight strength of 40. The shattering power or brisance (B) of an explosive is usually compared with TNT which is set at 100. The strength values of some explosives are listed in Table 14.4. Most of the explosives are about the same strength as TNT. The B is difficult to determine experimentally, and a proposed calculated value is

$$\mathrm{B} = d(\mathrm{VOD})^2 \tag{14.2}$$

where d is the density. Other expressions used to calculate B include a force factor, but experimental values are still the most reliable. The experiment called the *sand-bomb* test consists of 80 g of Ottawa sand—20 + 30 mesh placed in a heavy-walled cylinder onto which is placed 0.400 g of the test explosive. An additional 120 g of sand is placed on top, and the explosive is detonated. The mass of sand that passes through the +30 mesh screen after the detonation is the B.

14.4 Oxygen Balance

The detonation of an explosive is an oxidation reaction in which it may be assumed that all the carbon forms CO_2, all the hydrogen forms H_2O, and all the nitrogen forms N_2. On this basis, an explosive with the composition $C_xH_vO_zN_D$ will have an *oxygen balance* (OB) of

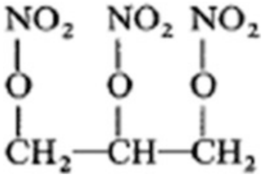
$$\mathrm{OB} = \mathrm{z} - 2\mathrm{x} - y/2 \tag{14.3}$$

A positive value indicates a surplus of oxygen within the explosive whereas a negative value indicates that oxygen must be supplied, usually from the surrounding air. The values are expressed in terms of moles of oxygen (O) per kg of explosive. Explosives are often blended to give an oxygen balance of zero or slightly positive value. Hence, Table 14.3 shows an amatol 80/20 with 4:1 NH_4NO_3:TNT which would give an OB of −46.2 + (4 × 12.5) or a total value of +3.8. The detonation of mixture of explosives is, however, not only dependent on the OB but also on the combustion reactions as well as other physical properties.

14.5 Modern Explosives

The secondary explosives listed in Tables 14.3 and 14.4 represent the more common compounds. Some comments on a few of these will illustrate their relative characteristics.

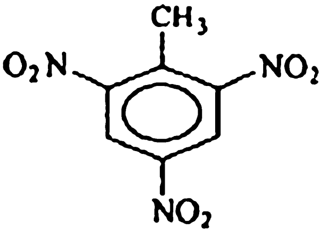
14.5.1 Nitroglycerin



This colorless oily liquid has a density of about 1.6 g/mL, a freezing point of 13.2°C, and decomposes before it boils at 1 atm. It is slightly soluble in water but much more soluble in acetone, ether, benzene, and chloroform. It is very sensitive to shock, especially when the liquid contains air bubbles. It is made by reacting glycerol with a mixture of HNO_3 and H_2SO_4 at -20°C.

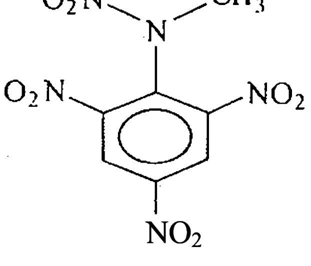
When *nitroglycerin* is adsorbed onto kieselguhr (25% diatomaceous earth, SiO_2), a plastic cheesy mass is formed. Present stabilizers use combustible material such as sawdust, flour, starch, or cereal products. When mixed with about 8% collodion cotton, it forms blasting gelatin. Plasticizers such as ethylene glycol dinitrate $(CH_2ONO_2)_2$ are added to reduce the freezing point of the dynamite and to increase its OB.

14.5.2 Trinitrotoluene (TNT)



Trinitrotoluene is easily made by the reaction of HNO_3 and H_2SO_4 with toluene. The order in which the reagents are mixed influences the output and safety of the process. It is thermally stable for over 40 h at 150°C and can be stored for 20 years at ambient temperatures. It is insensitive to shock and friction. It is slightly toxic at concentrations greater than 1.5 mg/m^3. Its use is extensive in the military as bombs, grenades, shells, torpedoes, and depth charges.

14.5.3 Tetryl



Tetryl, also called *tetranitromethylaniline*, has a melting point of about 130°C with some decomposition. It is nonhygroscopic and practically insoluble in water but highly soluble in acetone and benzene. It can be stored for over 20 years at ambient temperatures with no noticeable change in properties.

Tetryl is prepared by the nitration of dimethyl aniline followed by the oxidation of one of the *n*-methyl groups to CO_2 and more nitration.

Tetryl is used as a booster where it is mixed with TNT (called tetrytol) and some graphite to help pressing the mixture.

14.5.4 Ammonium Nitrate, NH_4NO_3

Ammonium nitrate is easily made by reacting nitric acid with ammonium hydroxide:

$$HNO_3 + NH_4OH \rightarrow NH_4NO_3 + H_2O \tag{14.4}$$

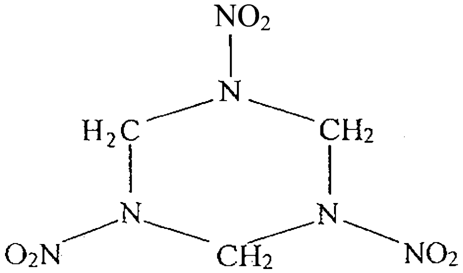
The reaction is exothermic and can be carried out in a borehole prior to its detonation. The thermal decomposition of NH_4NO_3 yields nitrous oxide, N_2O:

$$NH_4NO_3 \xrightarrow{220°C} N_2O + 2H_2O \tag{14.5}$$

The ignition temperature of NH_4NO_3 is about 465°C with heat of combustion of 2.62 kJ/g and an oxygen balance of +12.5 g/atom/kg. It is difficult to detonate, but accidental explosions of stored tonnes of the material on land or in ships have caused thousands of deaths and injuries during the last 100 years.

Its VOD is between 1.1 and 2.7 km/s. When fuel oil is added to the salt, it is known as ammonium nitrate fuel oil (ANFO). It is usually added to other explosives to increase the overall oxygen balance of the mixture.

14.5.5 Hexogen



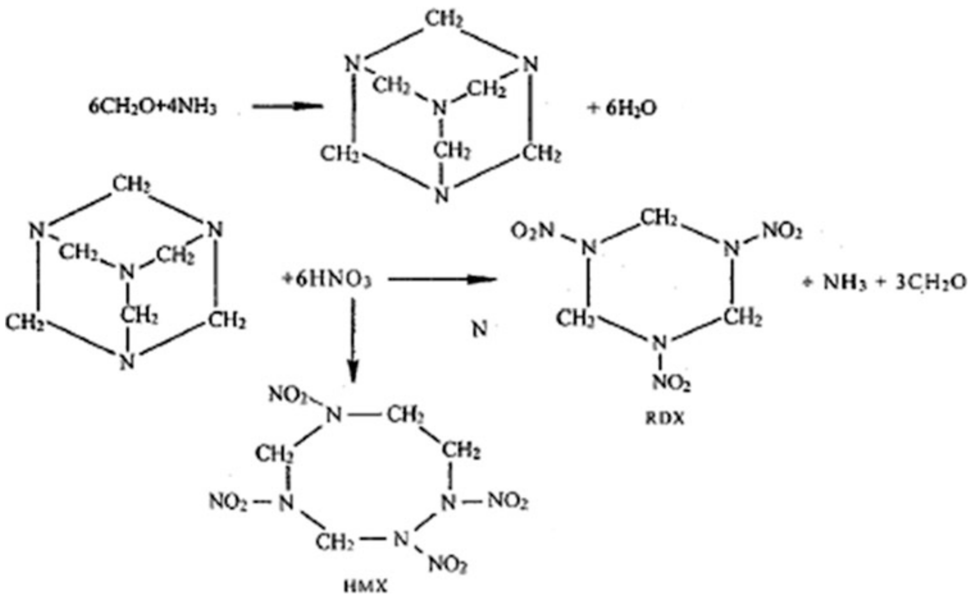
Cyclonite or *hexogen* (RDX) was first prepared in 1899 and was initially recommended for medical use. Later applications (1916) included its use as a smokeless propellant. During World War II, Germany manufactured 7,000 t of RDX per month, whereas the US production was more than twice this rate.

Table 14.5 Some propellants and selected properties

Fuel	Oxidant	Storage temp. (°C)	ΔH^0_{comb}(kJ/mol)	I_s (s)
Cryogenics				
H_2	O_2	−253/−183	−241.8	362
H_2	F_2	−253/−188	−271.1	352
Storables				
N_2H_4	H_2O_2	20/20	2686/N_2H_4	300
Ethylene oxide[a]		20	5237	170
Nitromethane[a]		20	675	220

[a] Monopropellants

This substance was the explosive of choice in the last world war. It is prepared by the reaction of ammonia with formaldehyde to form hexamethylenetetramine that when nitrated forms RDX with tetramethylene tetranitramine (HMX) as a by-product:



(14.6)

The fuels listed in Table 14.5 are practical propellants. More exotic choices such as diborane, B_2H_6; acetylene, C_2H_2; ozone, O_3; oxygen difluoride, OF_2; and nitrogen trifluoride, NF_3 are a few examples.

Solid propellants usually consist of ammonium nitrate (NH_4NO_3), ammonium perchlorate (NH_4ClO_4), and aluminum powder bound in a resin of polystyrene, polyurethane, or polybutadiene. Specific impulse values of 250–300 s are achieved depending on the choice of fuel and oxidizer.

14.6 Applications

Explosives and deflagrators are used in a variety of *applications* which include propellants, fireworks or pyrotechnics, welding, riveting, and cladding.

14.6.1 Propellants

In an age of rockets and space travel, there is a constant demand for new and stronger *propellants.* These are classified into cryogenics and storable liquids and characterized by the specific impulse (I_s) which is the thrust per unit mass flow of fuel and by convention reported in units of seconds (see Table 14.5). The thrust depends on the combustion temperature and the exhaust and combustion chamber pressures, P_E and P_c, respectively.

RDX is often mixed with TNT (60 RDX/40 TNT) to achieve a higher VOD and thus greater strengths. When mixed with lubricating oil (12%), it became the common plastic explosive of World War II. The plastic which does not lose its flexibility, C_3, consists of 77% RDX and 23% gel composed of dinitrotoluene, nitrocellulose, and dibutyl phthalate. The putty- or doughlike material has an advantage in demolition work by forming space charges which can slice through a steel pipe or bridge support.

14.6.2 Pyrotechnics

Fireworks usually use low explosives which are reliable, stable, and of low toxicity and reasonable cost. The original oxidizer (in black powder) potassium nitrate (KNO_3) is still in use today. Potassium perchlorate ($KClO_4$), ignition temperature 560°C, is much preferred over potassium chlorate ($KClO_3$) which ignites at 220°C when mixed with sulfur. The colors are obtained from the various salts: yellow is readily obtained from sodium salts (such as Na_3AlF_6 or $Na_2C_2O_4$) due to the 589-nm line. Red is due to the strontium salts such as $Sr(NO_3)_2$ and $SrCO_3$ which emits the 606-nm band from SrO whereas SrCl gives the 636–688-nm red bands. Green is produced from barium as the nitrate or chloride. The 505–535-nm band is due to emission by BaCl. Blue is due to cuprous chloride (CuCl) which has a flame emission in the 420–460-nm range. Since $KClO_3$ is unstable in the presence of copper salts, it is customary to use NH_4ClO_4 with $CuCO_3$.

The fuels consist of resins, charcoal, and sulfur. A typical aerial display shell used in fireworks is shown in Fig. 14.1. The black powder is the propellant which fires the shell to suitable heights. A fuse ignites and fires the various compartments to provide the colors and flashes in sequence.

14.6.3 Metalworking

The use of explosives in *metalworking* was initially employed in 1880 to make spittoons. Today, the missile and rocket industry use explosives to shape bulkheads, nosecones, and even large rocket sections. A small 50-g charge can do the work of a 1,000-t press shaping a thick metal plate 2–3 m in diameter. An example of a metal forming system is shown in Fig. 14.2. The dye is usually cheap material of concrete or plaster which can be evacuated. The sheet metal is held in place by a bed of water in which the explosive charge is detonated. The pressure and shock wave forces the metal into the evacuated mold in microseconds.

A less hazardous method is the use of an exploding wire to generate the shock wave. A thin resistive wire 0.03 mm in diameter is connected to a condenser (1–10 μF) and is charged to high voltage. When the condenser discharges through the wire, it explodes in microseconds creating the shock wave through the water bed. The method has been used in cladding and welding. For example, it is possible to apply a thin layer of platinum on a steel crucible which will have most of the properties of a 100% Pt crucible but which contains less than 5% Pt. Normally, the metal oxides on the surface prevent the two metals from bonding. However, the shock of the explosion forces the

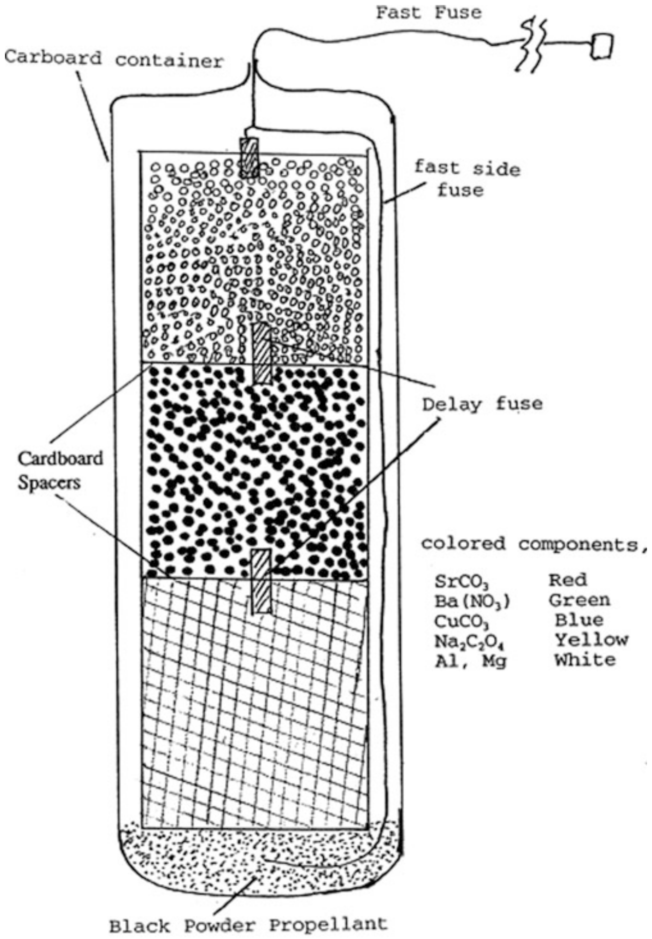


Fig. 14.1 Typical structure of an aerial shell for fireworks display. The compartments of the rocket usually produce different colored fireworks and patterns

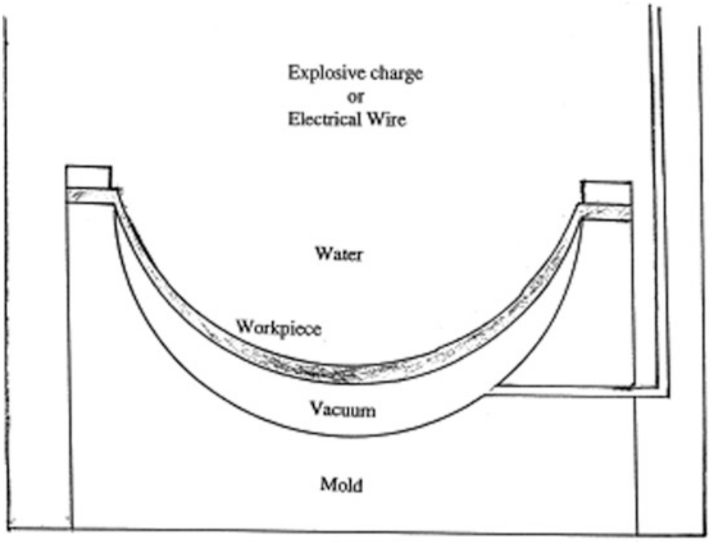


Fig. 14.2 Typical arrangement for explosive metal forming

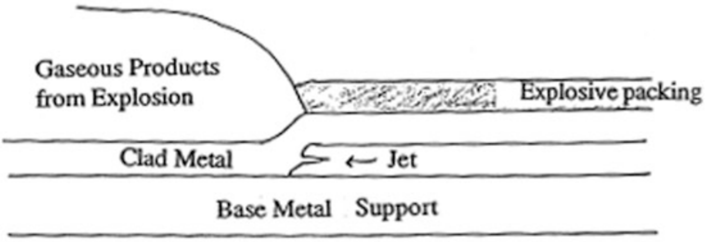


Fig. 14.3 Schematic diagram of the explosive cladding of a metal

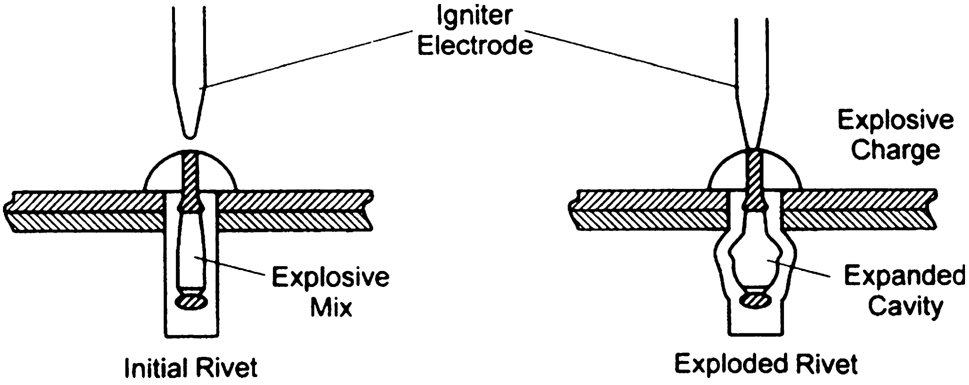


Fig. 14.4 Typical sequence of a riveting system

cladding metal onto the base metal under plastic flowing conditions, producing a metallic fluid jet at the point of contact (see Fig. 14.3). This removes the surface oxides leading to intimate welding of the two metals. The critical speed of the explosive weld is 200–300 m/s, and granular explosives are formulated to meet these requirements.

14.6.4 Riveting

Explosive *riveting* has been used for over 60 years and was originally designed for rivets where backup space was insufficient for normal processing. Applications include automobile brake shoes, aircraft industry, tanks, and other military vehicles.

The typical rivet is hollow and filled with explosive which can be detonated either thermally or by an electric charge. A typical sequence of explosive riveting is shown in Fig. 14.4.

14.7 Accidental Explosions

From the early days of black powder usage to the industrial revolution and the extensive mining of coal, *accidental explosions* have been a constant reminder of technological development. The dust of grain causes 30–40 grain elevators to explode each year in the USA. Coal mine explosions caused about 100 deaths/year during the period 1931–1955, and in spite of precautions and improved safety regulations in coal mines and grain elevators, accidents still occur which often take lives and cause millions of dollars in losses.

Table 14.6 Classification of accidental explosion

Type of explosion	Typical system and results
1. Detonation of condensed phase systems	
(a) Light or no confinement	(a) Blastwave: Manufacture, transport, and handling of explosive chemical reactors, distillation columns
(b) Heavy confinement	(b) Less damaging because of the design
2. Combustion explosions in enclosures	
(a) Fuel vapor	(a) Ignition source: building shops, boilers, low energy blast when length-diameter (L/D) = 1
(b) Dust ($d < 75$ μm)	(b) Usually ignited by another explosion, coal mines, grain elevators, pharmaceutical industries
3. Pressure vessels	
(a) Simple failure	(a) Vessel fails due to heat or corrosion, explosion in boiler due to steam or combustion
(b) Combustion generated failure	(b) Contaminated compressed air lines
(c) Combustion and failure	(c) Fireball due to stored fuel
(d) Failure after runaway chemical reaction	(d) Exothermic reaction (Bhopal)
(e) Failure after runaway nuclear reaction	(e) Chernobyl
4. Boiling liquid expanding vapor explosion (BLEVE)	Ductile vessel (tank car) with high vapor pressure combustible liquid. Fireball
5. Unconfined vapor cloud explosion	Ignited spills of combustible fuels
6. Physical vapor explosion	Island volcanoes, liquid propane on water

Table 14.7 Estimation of fuel mass from spherical fireball size

Fireball diameter D (m)	Fuel mass M (kg)	Duration t (s)	Power (GW)
25	80	2	1.6
50	640	4	6.9
75	2,160	5.8	15
100	5,125	7.8	28
125	10,000	9.7	43
150	17,300	11.6	62
200	41,000	15.5	110

There are many varied types of explosions which are accidental. A common classification is given in Table 14.6.

A fireball is the result of a fire causing a container, holding a large quantity of flammable liquid, to burst. The sudden release of the liquid which is vaporized by the heat results in a fireball of diameter, D, lasting for a duration of time, t. Independent of the fuel or heat of combustion, the relation between the size of the spherical fireball (diameter D in meters), the mass of combustible substance (mass M in kg), and the duration (time t in sec) is given by

$$D = 5.8M^{1/3} \tag{14.7}$$

and

$$t = 0.45M^{1/3} \tag{14.8}$$

which are based on previous accidental explosions. Some calculated values are shown in Table 14.7 and plotted in Fig. 14.5 on a semilog scale. The progress of the fireball and the structure is shown in

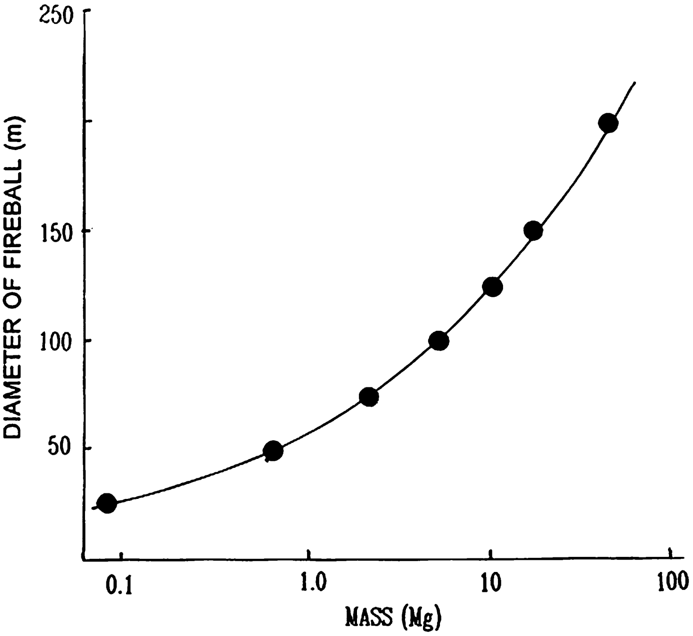


Fig. 14.5 Semilog plot of (14.7) from the data in Table 14.7 showing the diameter of a fireball as a function of the mass of fuel ignited

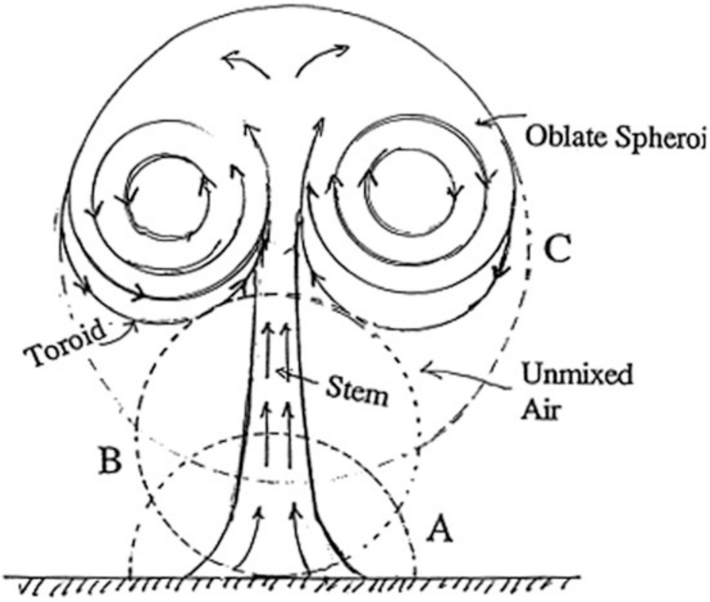


Fig. 14.6 Typical development of a fireball from *A* to *B* to *C* showing the stem through which the fuel is funneled

Fig. 14.6. As the pressure of the detonation products decreases to ambient pressure, the density of the gas decreases to less than that of the surrounding air, resulting in a buoyant force causing the fire to rise. The spherical shape is formed as the fuel continues to burn and becomes more buoyant. The spherical fireball then lifts from the ground, bringing in more air by convection and vortex motion.

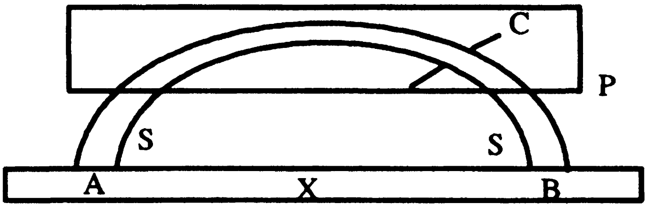


Fig. 14.7 An apparatus used to determine relative VOD

A stem is formed from the fuel spilled on the ground, creating a mushroom-type cloud. The spherical fireball changes into an oblate spheroid and then into a toroid, eventually consuming all the fuel and ultimately dissipating its energy.

Combustible vapors must be treated with care and respect. Standard precautions in design and construction must be followed, accidents anticipated, and provisions provided.

Exercises

1. Distinguish between an explosive and a detonator.
2. What chemical functional groups impart explosive properties to a compound?
3. Distinguish between a propellant and an explosive.
4. What is meant by the sensitivity of an explosive?
5. How is sensitivity to impact determined?
6. Define brisance and VOD.
7. How may the strength of an explosive be determined?
8. Write a short note on the application of explosives to metalworking.
9. Gunpowder consisted of 75% KNO_3, 15% charcoal, and 10% sulfur. Based on these properties, write a chemical reaction in which K_2SO_4 is formed instead of K_2S_2 in reaction.
10. The VOD of explosive *X* is determined relative to the standard explosive *S* (see Fig. 14.7). The explosive is initiated at *O*. At *A*, the standard explosive ignites as *X* continues to burn. When the burn of *X* has proceeded to *B*, then *S* ignites to meet the other flame front at *C* which is marked in a lead plate *P*. From the distances *AB*, *AC*, and *BC*, show that

    show that $$(\mathrm{VOD})_X = \frac{AB(\mathrm{VOD})_S}{AC - BC}$$

11. Calculate the specific volume of gas produced at STP per g of AgN_3.
12. The explosive HMX (cyclotetramethylene tetranitramine), $C_4H_8N_8O_8$, has molecular mass of 296.17 g/mol. Calculate its oxygen balance.
13. Compare relative calculated brisance from (14.2) with the values in Table 14.4.
14. What blend of RDX and NH_4NO_3 would give a positive value for an overall oxygen balance?
15. Construct a log-log plot of (14.8) using the data in Table 14.7.
16. A recent fireball due to the explosion of a solvent recycling plant was estimated to have a diameter of 75 m and to have lasted about 6 s. Estimate the mass of solvent ignited.
17. A train derailment in which liquid propane exploded formed a fireball of 250 m in diameter. Estimate the mass of propane burned and the duration of the fireball.
18. Calculate the standard enthalpy of combustion of liquid by mass and by volume: (a) hydrogen and (b) fluorine (see Table 14.5).

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