1

Historical Background

1.1 Introduction

Historically, mankind has tried to dominate both fellow human beings and other animals for as long as humans have been around. Some of this domination was achieved by killing other species. This had two aspects; survival and providing food.

Survival was dictated by the fact that many animals regarded humans as excellent sources of food and were quite capable of killing humans. Humans could have two approaches; avoid areas known to contain threatening species or produce devices – weapons – which would enable humans to kill the threatening animals. Humans then developed a taste for the flesh of some of the animals they had killed, thus increasing the sources of food available. As the human population increased, conflict between humans for food and territory increased, and so humans started to fight amongst themselves. By using weapons, humans could overcome physical disadvantages, and the optimum situation was to be able to kill your opponent before they could kill you.

The sword and lance effectively extended the human arm and kept your opponent at bay but, as lances became longer and longer, they became more unwieldy. A remote killing weapon was required. Simple javelins, which could be thrown at the opposition, extended the distance between opponents but required considerable physical stature and skill to achieve the correct flight trajectory for the javelin. Therefore, in order to overcome human physical limitations, mechanical advantage devices were used. The earliest weapons for remote killing were simple slings. These could carry a stone and were capable of accelerating it to high velocity by spinning the sling in a circle. When one of the supporting thongs was released, the stone would travel in an almost straight line from the point of release. Impact of the stone with an animal or human was capable of killing or injuring the animal.

With the development of wood manufacturing skills, bows and arrows became individual weapons or, when grouped together became a lethal hail of arrows which did not depend on the individual accuracy of the archer. The longbow was the ultimate in these weapons. Improved performance came when mankind developed stored energy devices, such as

Laser Ignition of Energetic Materials, First Edition. S Rafi Ahmad and Michael Cartwright.

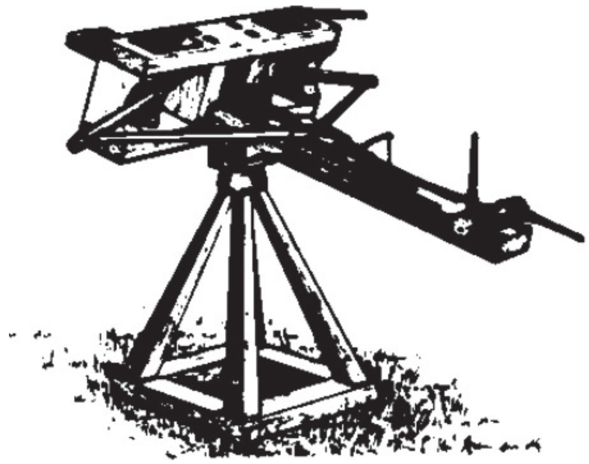

Figure 1.1 *Small-scale basic ballista. Reproduced with permission from Cranfield University © 2014.*

the ballista and crossbows, both of which stored mechanical energy in wooden elements but required winding up before loading the stone or arrow projectile. These overcame the limitations of physical stature required to effectively use the longbow. The ballista, Figure 1.1, was also used to fire barrels of burning oil at the enemy when they had formed shield walls against arrows. The oil container burst on impact and was one of the first deployments of pyrotechnics weapons.

1.2 The Gunpowder Era

Meanwhile, the Chinese were developing the first chemical explosive gunpowder. The earliest record of this was around 800 AD. Initially, the mixture was for use as a medicine but, as with all good inventions, serendipity intervened and a batch of the medicine fell on to the fire over which it was been cooked; it very rapidly burnt with a flash, smoke and rushing sound. The potential for this was recognized, and the Chinese started to use the mixture as a propellant for their lances/javelins. When attached to the normal throwing spear, these early rockets could extend the useful range of the javelin by as much as a factor of two.

It took about 400 years for the technology to appear in Europe, when a cleric Roger Bacon was credited with discovering the properties of gunpowder. He was so afraid of its properties that he hid the details of the composition in code in religious manuscripts. The recognition of its propellant properties resulted in the manufacture of muzzle-loaded cannons.

An idea of the chronology of the development of the science is given in Table 1.1 on page 3.

1.3 Cannons, Muskets and Rockets

The barrels of the first cannon systems were simple wooden devices made from hollowed-out tree trunks, which were wrapped with wet ropes for added strength. The development of bronze and cast iron technology led to the production of iron-barrelled guns, such as

Table 1.1 *Some significant discoveries in the history of explosives.*

Explosive	Credited to	Nationality	Date
Gunpowder	{Anon	(Probably Chinese)	Before 1000
	{R. Bacon	English	c.1246
First battlefield cannon		Italian	c 1326
Crecy bombard		English	1346
Hand cannon		Italian	c 1364
Leonardo's mortar	Leonardo da Vinci	Italian	c 1483
Mercury fulminate	Kunckel	German	c.1690
Picric acid[1]	Woulff	German	1771
Mercury fulminate percussion cap	Forsyth	Scottish	1825
Nitrocellulose[2]	{Pelouze	French	1838
	{Schonbein	German	1845
Nitroglycerine	Sobrero	Italian	1846
TNT	Wilbrand	German	1863
The fulminate detonator	Nobel	Swedish	1865
Dynamite	Nobel	Swedish	1867
Ammonium nitrate mixtures	Ohlsson & Norrbin	Swedish	1867
Tetryl	Mertens	German	1877
N.C. propellants[3]	{Schultze	German	1864
	{Vieille	French	1884
Ballistite	Nobel	Swedish	1883
Cordite	Abel & Dewar	British	1889
Lead azide	Curtius	German	1890
PETN	Rheinisch-Westfaelische Sprengstoff A.G	German	1894
RDX	Henning (patented by	German	1899
	Herz)	German	1920
NTO	von Manchot and Noll	German	1905
Tetrazene	Hoffman & Roth	German	1910
HMX			
Slurry explosives	Cook	USA	1957
Emulsion explosives			
PBX			

[1]Explosive properties of Picric acid were not investigated for a further 100 years.
[2]Pelouze produced NC but did not understand the chemistry whereas Schonbein correctly identified the chemistry and made some propellant uses.
[3]Schultze produced the first successful powdered NC propellants and Vielle was credited with the first NC propellants for rifled barrel guns.

the Bombard, used at the battle of Crecy in 1346 (shown in Figure 1.2). This weapon used solid projectiles in the form of either suitable stone or cast metal (e.g. iron) spheres. The development of these weapons resulted in the foundation of the Board of Ordinance in 1414. The operators of these weapons were known as Bombardiers – a term still used for an artilleryman with the rank of corporal in the British Army.

In the fifteenth century, cannon were also deployed at sea on warships and these enabled the opposition to be destroyed at distance without needing to engage in hand to hand combat. A number of cannons were deployed along each side of the ship, and a broadside

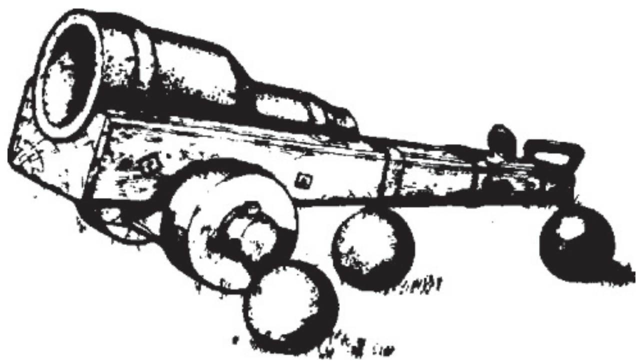

Figure 1.2 Crecy bombard 1346. Reproduced with permission from Cranfield University © 2014.

could be loosed at the opposition. Typical cannons are shown in Figure 1.3, which displays a typical army cannon in the foreground and a naval cannon in the background.

The naval cannon was mounted on a four-wheeled trolley rather than the two wheels of the army. This provided better stability onboard a ship in heavy seas. The iron guns were made of a number of staves, or bars, of iron which were formed into a cylinder around a mandrel. Collars and hoops of wrought iron were heated and slipped over the cylinder. As these cooled, they contracted to form a reinforced tube. Surprisingly, breech-loaded cannon (often regarded as a modern invention, introduced when screw cutting technology was developed during the Industrial Revolution) were available in the early fifteenth century. The early systems used a simple hollow steel tube mounted on a wooden trough, with a space between the end of the metal tube and the end of the wooden support. A closed metal cup containing the propellant charge was then inserted into the gap and rammed into the rear open end of the barrel. The system was then sealed by inserting a wooden plug behind the charge-bearing cup to ensure the cup remained in place when the gun was fired. The components are displayed in Figure 1.4.

Figure 1.3 Showing a field gun in the foreground and a naval gun in the background. Reproduced with permission from The Mary Rose Trust. © The Mary Rose Trust, 2014.

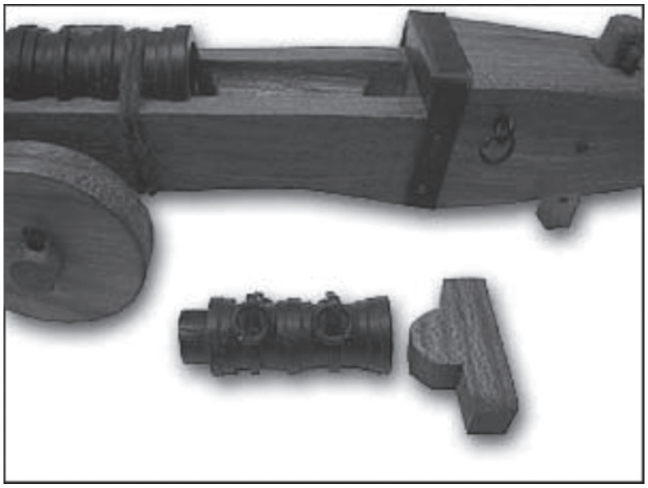

Figure 1.4 *Showing active region of a breech-loaded cannon as used on the* Mary Rose. *Reproduced with permission from The Mary Rose Trust. © The Mary Rose Trust, 2014.*

Although the breech was by no means gas-tight, these guns were powerful enough to inflict heavy damage on another ship at close range. This has been demonstrated in field trials using a replica iron gun. Later breech-loaded cannons were cast metal closed tubes, but with a slot in the side into which the charge could be inserted and sealed in position again with a wooden plug. These were more durable than the wooden supported systems. The beauty of the system was that each gun had a number of charge cups which could be filled with gunpowder prior to engagement, so that a higher rate of fire could be produced. Also, swabbing out of the gun between shots was not so crucial, since the next charge did not have to be loaded down a barrel which could contain hot residues, liable to ignite the charge before the gun was ready. This, again, increased the rate of fire. Notice that the ignition of the charge was by transmission of an externally generated flame through a touch hole. This hole allowed some of the burning gases to be vented, thus reducing the gas propulsion of the projectile and also blowing hot embers back towards the gun crew.

As well as the standard stone or iron shot, these guns could fire a vicious Tudor version of canister shot consisting of chopped flint stones. These were particularly useful when the opposing forces had a number of soldiers exposed on an open deck.

Gunpowder was the propellant in cannon for the next 400 years, but it was the longbow that was responsible for English superiority at the battle of Agincourt 1425. Cannons were mainly used as siege weapons, and they required skilled operators to achieve success with the minimum number of shots. Several options were proposed by Leonardo Da Vinci to alleviate some of the requirement for skilled operators, and he proposed a multi-barrelled system, as shown in Figure 1.5, which provides sketches from his work book.

One of the most fearsome siege weapons was the Dardanelles Gun. This was a cast bronze weapon weighing over 18 tonnes, and it was five metres long when assembled from its two parts, which screwed together. ‘Superguns’ were not a modern invention, but only became practical after the Industrial Revolution. The solid cannonball weighed about 400 kg could penetrate over one metre thick walls with an effective range of almost a

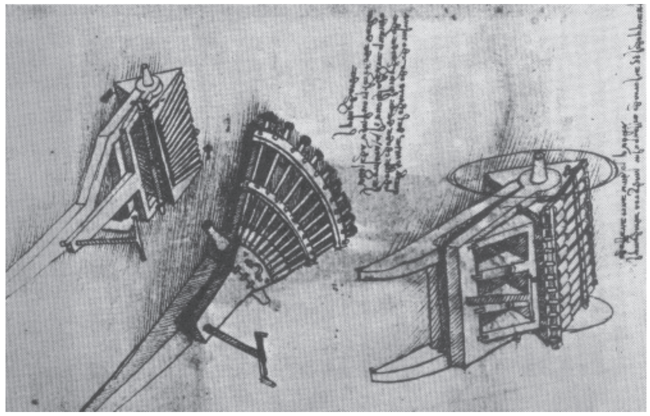

Figure 1.5 *Leonardo Da Vinci's sketches for multi-barrelled cannon systems.*

kilometre. Leonardo also proposed mortar-type guns for siege work on the principle that, if it was not possible to penetrate the wall, fire over it. Two mortars from his original designs are depicted in Figure 1.6. They could both fire single or multiple flint stone solid shot. Note on one of the mortars the sophistication of the range/angular adjustment and also the rudiments of sighting instruments

This attention to cannons resulted in the creation of the first body of specialist artillerymen, The Guild of St George (1537), which became Honourable Artillery Company in 1668. The gunpowder was of variable performance because of three factors. Solids had to be ground to the correct size and then correctly mixed in the correct proportions, which was, according to the early Chinese formulation, equal parts of brimstone, (sulfur), charcoal (carbon) and saltpetre (potassium nitrate). Small particle size materials, which produced

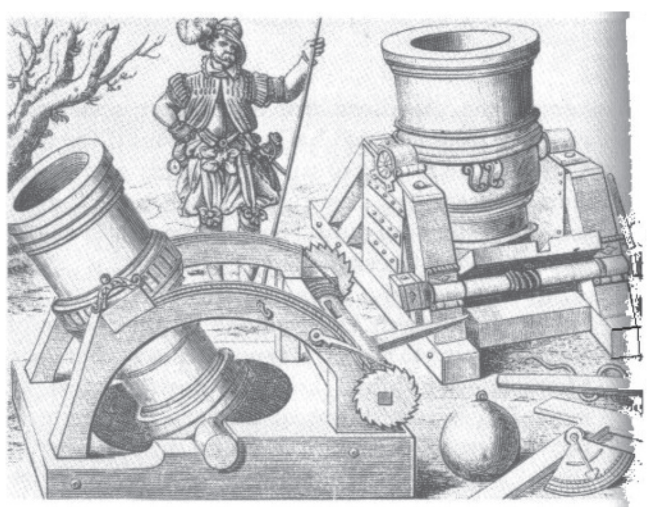

Figure 1.6 *Leonardo Da Vinci-designed siege mortars.*

the optimum gun performance, were very dusty, and hence the millers worked outdoors whenever possible. Note that the ingredients were ground separately, since it was discovered early in the use of gunpowder that grinding all the ingredients together resulted in ignitions, with serious consequences. It was only with the development of the 'Corning process' that the dust problem was reduced. In corning, the finely divided powders are mixed with water to a paste, which is spread out and dried to a cake. The cake is then broken into smaller fragments (≈ 1–2 mm diameter), which can easily be filled into bags to load into cannons.

Because of the difficulties recruiting skilled artillerymen, alternative siege weapons were developed. The Petard was essentially a barrel of gunpowder fitted with a slow match fuse and was carried into battle by a Petardier. At some suitable stage, he would rush forward and place the Petard against the wooden gates of the fort, light the slow match and retreat as fast as possible. If the slow match was badly made, it would burn rapidly, ignite the charge before the Petardier had retreated and he could be killed by the gunpowder explosion. Hence the expression 'Hoist by ones own Petard'.

The first explosive charges fired from guns were containers of gunpowder fitted with a slow fuse which was ignited by the burning gunpowder propellant charge. This was again a very hazardous operation, since most of the containers did not survive the ignition of the gunpowder propelling charge, so they were effectively an added propellant system with no useful performance. Thus they were very unpopular with artillerymen.

1.3.1 Musketry

Over a period of time, the gunpowder system was adapted to personal usage in the form of the musket. Again, this was muzzle-loaded and fired solid shot from a smooth-bore barrel. The gunpowder charge was poured into the barrel from a powder horn, and packed down using a cotton wad to retain the powder and a ramrod to force the charge into a compact charge before inserting the ball shot. The shot would be also rammed in, to prevent it from rolling out if the gun was pointed downwards. The internal charge was set off by igniting a small gunpowder charge contained in a cup on the outside of the barrel, and the burning process was transferred through a touch hole into the interior. This firing hole was a source of reduced performance, since some of the gases produced inside the barrel could vent to the outside, thus reducing the gas pressure driving the ball.

Because the escaping gases could burn the firer, some of the heavier muskets were mounted on a crude stand so that the weapon could be fired at arm's length, reducing the hazard to the operator. The firing charge was set off by a range of devices. The first initiation device was a glowing length of burning rope, which was applied either manually or by a rotating arm carrying the 'slow match' – a 'matchlock' device. A series of alternatives were developed, including a flint being struck against a hard surface, causing a spark which ignited the gunpowder in the pan or cup – 'the flintlock'. The basic flintlock and the adapted wheel lock are shown in Figure 1.7.

If the material in the cup ignited, but failed to set of the main propellant charge, then it gave rise to the term 'flash in the pan' for a trivial output of no use to the firer. This situation left the gun in a dangerous condition which required careful re-priming. A later stage development came in 1805 when another clergyman, Alexander Forsyth, produced a metal cap which contained a sensitive composition, mercury fulminate. The cap covered the touch hole, as shown in the lower image of Figure 1.7, and was initiated by a mechanical

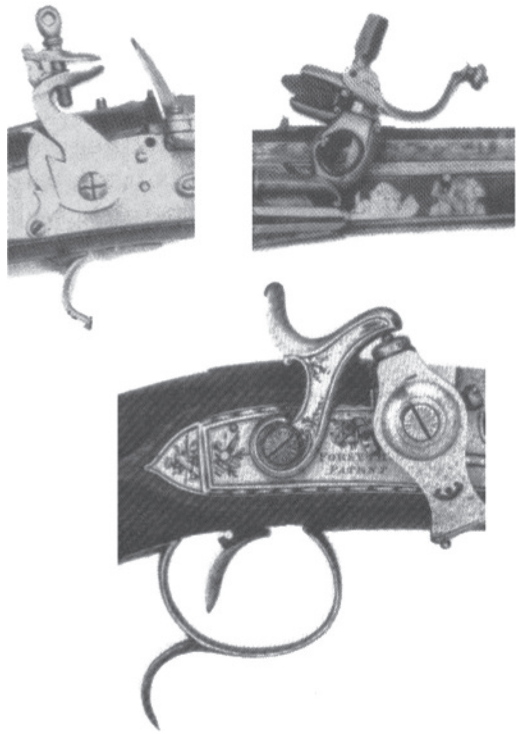

Figure 1.7 *Showing ignition systems in musketry. Top left: original flintlock. Top right: wheel lock. Bottom: first percussion cap system. Reproduced with permission from Cranfield University © 2014.*

blow delivered by a hammer striking the outside of the cup. The mercury fulminate reliably delivered an explosion to set off the charge at the rear of the barrel. This dramatically reduced the firing time between the operation of the trigger and the ejection of the projectile. The cup provided a partial seal against gas venting through the fire hole, thus increasing the gas pressure driving the musket ball. The cap system also increased the kickback on the weapon, since momentum must be conserved during the firing. If the bullet exited the barrel with greater velocity and momentum, then the rearwards velocity of the gun also increased.

Note that, at this stage, the projectiles were still solid, with no explosive properties, and that the wadding was important because the shot was a poor fit in the barrel, due to manufacturing problems. After the English Civil war in the mid-seventeenth century, which led to the establishment of a permanent army under the control of Parliament, the development of the musket accelerated. Also, in 1671, the government purchased the Woolwich site for their armaments, and this became Royal Arsenal 1805. This site provided fireworks for the celebration which accompanied Handel's Fireworks Music.

One example of the devastating performance achieved with gunpowder muskets was the 'Brown Bess' used by the English army at the battle of Culloden in 1746, when it was trying to subdue the Scottish rebels. The solid, $\approx$ 20 mm diameter, musket ball was lethal to 100 m in the hands of a skilled musketman, and a volley of shots could decimate an advancing force of soldiers armed with swords and lances. Typical shields of the time, a metal skin on a wooden backboard, offered little protection and, as recent trials have demonstrated, the same musket ball could pass through the shields and bodies of two soldiers standing one behind the other.

Prior to 1759, the Board of Ordinance did not make gunpowder but used the East India Company as suppliers, and they often sourced their supplies from the French Arsenal in Paris. Antoine Lavoisier, of combustion theory fame, was the administrator, and he ensured that good quality control was applied at all stages – hence, French gunpowder was the best available in Europe. In 1759, the Board of Ordinance purchased Faversham Kent powder mills. The factory blew up 1781, and the Board then bought the Waltham Abbey Powder mills in 1787 to continue the supply. Around this time, another cleric, Bishop Watson, obtained charcoal from distilling wood in closed vessels. This increased purity charcoal gave $\approx 70\%$ improvement in performance. The explosion at the Waltham Abbey Powder mills in 1843, which resulted in many fatalities, was one of the driving forces for the development of alternatives to gunpowder and the first efforts with nitrocellulose. Modern gunpowder mills are subject to very stringent safety measures.

1.3.2 Rocketry

Some military men used rockets, with cutting blades attached to the front, essentially to increase the range of the weapon over the musket and thus keeping the musketeers out of musket range. However, their flight was very unpredictable because of the uneven burning of the gunpowder, and also steering was purely by having the centre of mass behind the centre of thrust, which state was achieved by attaching the rocket to the front of a long, solid wooden stick. This stick added considerable mass to the projectile, reducing its range. Most of these devices flew along spiral paths. The conflict in India in the eighteenth century saw the Indian forces using batteries of rockets in the battle of Guntar against the advancing English infantry to great effect, both from a lethal viewpoint but also from a psychological viewpoint, since the rockets made screaming sounds as they passed through the air.

After the battle of Seringapatam in 1799, Congreve developed rockets and explosive missiles with ranges of up to 3,500 metres. In 1806, these were used to attack a French flotilla in Boulogne, destroying many of the ships and blocking the harbour. Similar devices were used at the battles of Copenhagen and Walcheren, with similar results. The inaccuracies of the rocket system did not matter; because of the extended target area and the density of the targets, they were bound to hit *something*, even if it was not what was aimed for. At the battle of Leipzig in 1813, rockets were used by the army. Congreve's rockets were used by British Army until 1865, when Boxter invented an improved type. In 1845, Hale invented fin-stabilized rockets, avoiding the useless mass of the guidance stick.

1.4 Explosive Warheads

The first steps along the path for explosive warheads came with the development of the grenade. This was a container, usually of wood or metal, which contained a gunpowder charge, with or without some added musket balls and a length of burning fuze, initially a slow match. As the two sides involved in the conflict approached each other, grenadiers would light their fuzes, charge towards their opponents and hurl the grenades into the ranks of the opposition. Sometimes, the thrower would make use of the old sling technology to

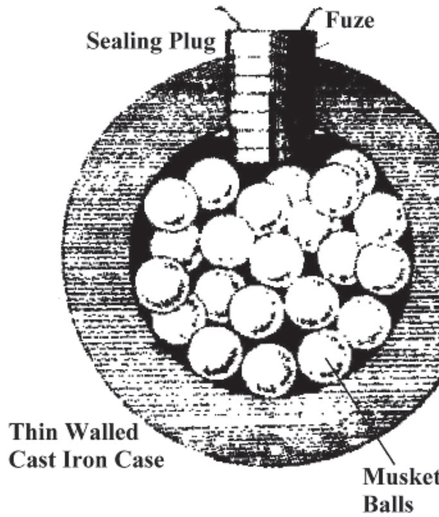

Figure 1.8 *Shrapnel's exploding cannon shell ≈ 1780. Reproduced with permission from Cranfield University © 2014.*

increase the effective range over which the projectile could be hurled. The hazard of this job was again reflected in the recognition of the Grenadiers regiments being the leading soldiers in any parade, standing to the right of the line. There was a small financial reward to grenadiers, but it did not compensate for the high grenadier mortality. Opposition riflemen could easily identify the grenadiers and concentrate their firepower on them.

At this stage, two developments occurred which had a significant effect on the effectiveness of both guns and rockets. Colonel Shrapnel designed a cast iron hollow sphere which was packed with musket balls and gunpowder, with the filling hole being sealed by a pyrotechnic delay device, ignited by the output from the gunpowder propelling charge. The system is shown in Figure 1.8.

The system originally blew out the plug and the musket balls through the plug hole, giving a shotgun effect, but the later system was designed to shatter the case and scatter case and musket balls in all directions. If the delay element was correctly assembled, the gunpowder contained in the shell was initiated by the delay just as the projectile arrived at the opposition, explosively bursting the casing and thus showering the opposition with the musket balls. If the delay operated while the projectile was still in the barrel, then it behaved rather like a large-scale modern-day shotgun. The modern term 'shrapnel' is applied to any fragment from the warhead.

Congreve applied the same strategy to his rocket systems, using a similar warhead, as shown diagrammatically in Figure 1.9. One advantage of this system was that, because the delay was at the end of the rocket motor, the problem of sealing the delay against propellant gas pressure was minimized. Also, the rocket was down range before the warhead exploded if the fuse was badly fitting. The technology was very imprecise and only rarely did they achieve their design operating conditions. Nevertheless, the foundations were laid for further developments in the field of explosives. The development of rifled gun barrels

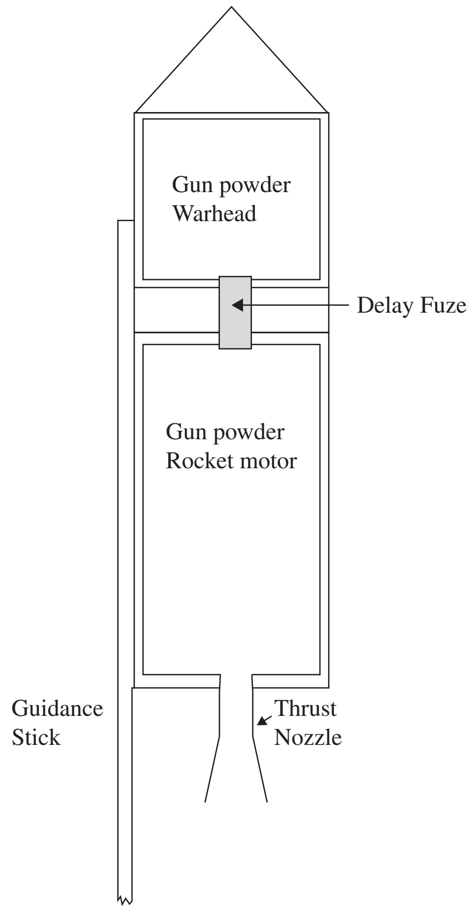

Figure 1.9 *Congreve's exploding warhead rocket.*

led to the demise of unstable rocket systems until the Second World War, when the use of anti-tank rockets by both infantrymen and aircraft used double-base propellants and were fin-stabilized. Now they are the principal air-launched weapon for both ground attack and aircraft self-defence, as well as ground-to-air defence. Naval Maroons are modern variations of the Congreve system.

1.5 Explosives Science

While all these developments in gun and rocket technology were taking place, the science of chemistry was quietly developing in some surprising directions. Instead of trying to turn everything into gold, as per the alchemist's dream, some people started to look at the changes which could be induced in the world around them. Metals which could be simply manufactured by roasting on fires with or without the assistance of charcoal had been around for some considerable period of time, and some chemists were starting to look at non-metallic materials. The discovery of strong acids such as sulfuric, hydrochloric and nitric acids led to a number of chemists experimenting with these materials to see what happened.

The first such experiment of significance to the explosives community was that performed by Kunckel, in Germany around the turn of the seventeenth century. He wondered what would be the effect of mixing ‘liquid silver’ – the metal mercury – with nitric acid in the presence of alcohol, which he had distilled from fermented wines. He obtained a white powder which showed many remarkable properties, as well as exploding at the slightest touch. He shelved the experiments, recording that the work was too dangerous for him to pursue. He had inadvertently made fulminate of mercury, which we now know as mercury isocyanate.

Later on, Woulff experimented with the effect of nitric acid on one of the products he had isolated from coal tar – phenol. He produced another explosive material, picric acid, trinitro phenol, which again could produce nasty accidents when impure or in contact with some metals, notably the lead used to make many laboratory vessels before the development of suitable glass devices. The technology was put aside for over one hundred years, before resurfacing during World War I, when picric acid was an alternative filling to TNT in munitions until its inherent safety problems resurfaced. Today, the lead salts of picric acid are used in initiating systems.

By the early nineteenth century, chemistry was developing at a very rapid pace. Early experiments on the reaction of nitric acid with cellulosic fibres were undertaken, and the first preparations of nitrocellulose achieved. It took a decade for the science involved to be correctly enunciated, and a further two decades before it was identified and trialled as a gun propellant replacement for gunpowder, which was inefficient, hazardous to handle and produced a significant quantity of unavoidable smoke. In a famous painting depicting the battle of Waterloo in 1815, much of the battlefield is obscured by the gunpowder smoke.

Shortly after the work on nitrocellulose, an Italian Professor, Ascanio Sobrero, worked on the effect of nitric acid on another natural organic oil, glycerol. He manufactured nitroglycerine and, having had a number of near misses with his students, he put the work to one side. In the meantime, civil engineers were starting to tunnel through rock to build railways, and the gunpowder available was only marginally better than men with picks and shovels on the hard granites encountered. Thus, for the first time in almost a thousand years, non-military people were driving the development of explosive technology. It was found that nitroglycerine was a powerful explosive, capable of shattering the hardest rocks. Unfortunately, it was also prone to accidental ignition, with fatal consequences. Immanuel Nobel and his son Alfred started to manufacture nitroglycerine at their plant in Helenebourg. Their success as suppliers of blasting explosives to the civil engineering industry was blighted by two problems:

1. It was very prone to accidental initiation.
2. It could be very unreliable when used in boreholes.

The first problem came to a head in 1864, when an explosion destroyed the Nobels’ manufacturing plant and the second problem indicated the solution to the first problem. The liquid nitroglycerine could be absorbed into porous rocks, thus reducing its effectiveness in bore holes. The Nobels recognized that other nitroglycerine-absorbing materials, such as certain types of diatomaceous earths (e.g. Keiselgur and also Fuller’s earth) produced materials which still had an explosive performance but were less hazardous in operations. These were identified as Guhr dynamites. nitroglycerine, when absorbed on these materials, was then comparatively safe to handle, but now was difficult to set off or initiate. Simple match fuzes no longer worked, so the Nobels, in 1865, turned to the work of Kunckel with mercury fulminate and used this compound in copper tubes to initiate their Guhr dynamites. They had developed the world's first detonator device.

The Nobels also discovered that nitroglycerine could react with nitrocellulose NC to produce a jelly-like material, which had lost the sensitivity of nitroglycerine but was still sufficiently explosive to be useful in rock blasting and gave reliable performance. The term gelatine dynamites was coined for these materials. It was also in the 1860s that nitroglycerine was trialled as the first replacement for gunpowder. The development of engineering skills produced higher-precision gun barrels and also the opening and closing breech devices, enabling a change from muzzle-loading systems to breech-loading and, with the development of the rifled barrel to spin stabilize the projectile, a step up in the performance of artillery was produced.

Whilst Nobels were working with nitroglycerine, Wilbrand was experimenting with concentrated nitric sulfuric acid mixtures on a number of hydrocarbons, the most important of which was toluene. As a result, he discovered trinitrotoluene or TNT – a most important explosive material, mainly because of its ease of handling. When melted in hot water, Liquid TNT could be readily cast into shells and be allowed to set. The problem of it cracking and other filling defects took a while to recognize and treat. The other advantage of TNT was that it had a good safety record, because it was difficult to set off accidentally. However, there was a downside to TNT which took longer to recognize. It is very toxic, and has appreciable vapour pressure when heated at its melting point. As a result, a number of people died during the early part of the twentieth century due to TNT poisoning. The environmental impact of the manufacturing process was also quite a problem, due to the red water produced during the purification process. This was left in lagoons to age, but bacteria struggle to digest TNT at above 200 ppm in solution – far below the red water nitrated toluene levels.

Further developments in chemistry lead to the production of further explosive materials, all of which gave enhanced performance. Lead azide became the detonator of choice, replacing mercury fulminate, and PETN (see appendix for it systematic name) was a booster designed to give reliable initiation of the high explosives. During the two world wars, chemical engineering technology was developed and applied to enable mass production of explosives – mainly TNT. In 1914, world wide production of TNT was $\approx$ 100 tons per annum, but by 1917 this had increased to $\approx$ 750 000 tons per annum. The Great War also accelerated the search for new, more powerful explosives, such as RDX and HMX. During the Second World War, rockets powered by NC-based propellants came into use again, either as area weapons (exemplified by the German multi-launch Nebbleweffer rocket battery) or air-launched systems used against armoured vehicles. Also, the first infantry, hand-launched, rocket-powered anti-armour weapons appeared. Following the two world wars, attention turned back to civilian demands for safer explosives to be used in quarrying and civil engineering.

The quickest way to dismantle a building is by the use of explosives. Engineers had to store gelatine dynamites in special stores, and the search for alternatives which did not pose such a serious hazard was instigated. Ammonium nitrate (AN)-based systems started to develop, particularly for quarrying operations, where the exposed nature of the sites posed considerable explosive storage problems. AN-based systems had the advantage of being cheap, since they were bulk manufactured for agricultural uses as a fertilizer. Simple mixtures with fuel oil, ANFO, which had been discovered about one hundred years previously, were early successes, and later systems such as emulsions, slurries and gels developed during the latter half of the twentieth century. The slurries and gels were often supplied in the form of sausages in plastic skins, of various diameters, which could be readily stored and packed into boreholes in mines and quarries. Also, some of the systems could be manufactured on site on demand. As a result, quarries did not have to store explosive compounds.

This is not to say that AN is not explosive, but that it requires special conditions and initiation with a booster before it will explode. This fact was very dramatically demonstrated at Oppau in Germany. An attempt to beak up the cake formed on the surface of a pile of AN stored outside with an explosive charge resulted in the complete detonation of the whole pile, causing many fatalities and devastating damage for several miles.

The drive to improved performance and safety has led to a number of newer explosive materials which will be identified in a later section. Military users have now realized the potential benefits of designing munitions which can not function accidentally but only on specific demand and, as a result the use of laser initiation, has a critical role to play in insensitive munitions (IM). To this purpose, encasing the explosive in a plastic matrix has reduced the occurrences of accidental initiation. Previously, RDX had been desensitized by using cast formulations with TNT, but the limit was 25% TNT, because of the problem of wetting the RDX solid. Even this level required very careful manufacturing methods to exclude trapped air. The other problem was the reduced performance of the mixture due the extreme oxygen deficiency of TNT. Casting the RDX with a polymer binder allowed almost 90% RDX levels. By using energetic binders, the loss of performance from pure RDX and HMX could be minimized. More will be discussed on this area in the a later section. The *in situ* manufacture of the polymer was not without problems, both from the presence of unwanted side reactions but also from the toxicity of some of the cross-linking agents used, for example, di- and tri- isocyanates.

Due to increasing concern for the environment, a search is on for replacements for heavy metal salts such as lead azide and styphnate, and also less toxic high explosives. Nitrotriazalone NTO, which was first prepared and characterized in the early twentieth century, has started to be evaluated. While NTO is marginally lower in performance than RDX, it is much less sensitive than RDX and is easier to manufacture in high purity. It is very soluble in water and, very importantly, its toxicity is several orders of magnitude less than RDX or TNT. The toxic level for animals is $\approx$ 10 g per Kg body mass, and bacteria can readily digest NTO. Other materials are being evaluated and, again, will be discussed in later sections.

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