HIGH EXPLOSIVES AND PROPELLANTS

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SECOND EDITION

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Preface to the First Edition

THE writer of a book on explosives is immediately faced with a difficult task of selection. He must decide what relative importances to place on military compared with commercial explosives, and on theoretical against practical aspects of the technology.

The quantity of military explosives made in the Second World War exceeded the total ever made for peaceful use by mankind. On this count it could be argued that military explosives should occupy a major portion of this book. On the other hand, wars are fortunately relatively shorter in duration than peace, so that at any particular time a reader is likely to be interested more in commercial explosives than in military.

More important, however, is to consider the contributions—good and bad—which explosives have made to the history of mankind. Any real assessment of this must show that the benefits which explosives have produced far outweigh their misuse in military pursuits. The explosives technologist, who has usually seen and perhaps even experienced the effects of explosives, is the last to want war or to want his products to be used for warlike purposes. It is no accident that Nobel, who founded the modern explosives industry, also founded the Peace Prize associated with his name. In this book the writer has followed his instincts and given pride of place to commercial, beneficial applications of explosives.

The writer has also dealt in greater detail than many authors would on the more fundamental aspects of his subject. He believes that the reader will be more interested in understanding the bases of the design and performance of explosives than in learning details of individual compounds or devices. If readers consider that the balance is wrong, the writer can only plead that there are no comparable books on the subject with which comparison could be made.

In deference to the wishes of the publishers, references in the text have been kept to a minimum and where possible to books thought to be freely

available. The writer has, however, included a short bibliography to Chapter 2, because he is not aware of any general reference of recent date which covers the whole ground adequately.

This book is concerned with the British explosives industry. Practice in other countries has been discussed only when the comparison is thought to be of value. That is the intention of this series of books and is not in any way intended to decry products which satisfy well requirements in other, often widely different conditions.

Acknowledgements are gratefully made to the following for permission to reproduce items from other books: Oliver & Boyd—Fig. 4.1, Newnes—Fig. 7.2; I.C.I. Ltd.—Figs. 14.8 and 14.9; Elsevier—Fig. 19.5; Interscience Publications—Table 17.1; Temple Press—Table 19.3.

Thanks are also due to the writer's many colleagues in the Nobel Division of Imperial Chemical Industries Ltd. for helping, knowingly and unknowingly, in the preparation of this book.

S.F.

Preface to the Second Edition

IN PREPARING the second edition of this book the opportunity has been taken to add sections on slurry explosives and a short account of "Nonel" fuse. Parts which were badly out of date have been modernised, and the opportunity taken to correct some errors and ambiguities. Thanks are again due to my former colleagues in NEC.

S.F.

Please Read This

Do not experiment with explosives or pyrotechnics.

In this volume a considerable amount of information is given on methods of making explosives and pyrotechnics. The book, however, does not attempt to say how these manufactures can be carried out with safety. The writer and publisher would be most distressed if this text led to a single accident by causing any reader to do experiments on his own.

In this country all preparation of explosives, fireworks, rockets and similar devices is illegal unless carried out in a duly authorised establishment.

Throughout the world explosives manufacturers have amassed many years of experience and have spent many millions of pounds to ensure as far as possible the safety of those working for them with explosives. Even so, accidents still occur with distressing injury and loss of life. Where these companies cannot succeed the amateur would be foolish to try.

Do not experiment with explosives—the odds are too much against you.

ERRATUM

Page 50 lines 6 and 7 from the bottom should read:

"explosives can be considerably improved within their
resistance to water by adding one or other of certain
well-known waterproofing agents. These"

CHAPTER 1

Introduction

AN EXPLOSION occurs when energy previously confined is suddenly released to affect the surroundings. Small explosions, like the bursting of a toy balloon, are familiar and innocuous, but large-scale explosions, like an atomic bomb, are rare and usually disastrous. Between these two extremes lie the commercial and conventional military fields where explosions are produced on a limited scale to cause specific effects. It is with explosions of this intermediate scale that this book is concerned.

It is unfortunately true to say that the views which most people hold on explosives stem either from first-hand experience of the effects of explosives used during times of war, or from reports of these effects. For military purposes explosives are required to cause destruction and are used in quantities so large or in such a fashion that destruction is inevitable. As a result, the impression is given of an overwhelming force causing uncontrolled devastation.

Yet, in truth, explosives can be used as a controlled and rather precise means of applying energy to a particular system. Many tons of explosive may be used in a single blast at a quarry face, yet the only visible effect will be for the face of that quarry to slump to the ground. It would be bad practice indeed if rocks from that quarry face were thrown any distance across the floor of the quarry or the neighbouring countryside. When an explosive is fired on the surface of a piece of steel, it will harden that steel to a predetermined depth without either breaking the steel or causing any noticeable deformation. The design and application of explosives is a science and explosives are as capable of control as are other products of industry.

Although all explosions are sudden releases of energy, the converse is not true and not all sudden releases of energy are explosions. By common

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consent, the term explosive is defined to exclude such items as bottles of compressed gas, even though these are capable of exploding on rupture. For the purposes of this book an explosive will be taken to mean a substance or mixture of substances which is in itself capable (1) of producing a quantity of gas under high pressure and (2) of being able to produce this gas so rapidly under certain conditions (not necessarily those of practical use) that the surroundings are subjected to a strong dynamic stress.

The burning of oil in a lamp is a slow process, the rate being determined by the need for the oil to evaporate and for the vapour to mix with the surrounding air to form a combustible mixture. To speed up the rate of combustion, it is necessary to disperse the oil in air before ignition. In a motor car, petrol in the carburettor is mixed with the right amount of air so that when ignited in the cylinder it explodes. Such gaseous mixtures are effective explosives but suffer from many disadvantages, of which the most important is the small amount of power available from any given volume. To obtain a better power ratio it is necessary to use solids or liquids.

The first step in producing more rapid combustion in a condensed phase is to provide a solid which will replace oxygen from the air in supporting combustion. The use of nitrates for this purpose has a long history and it is probable that the stories of old Chinese explosives and of Greek fire relate to combustible mixtures to which nitrates had been added to make their reaction more intense. The first real record of an explosive, however, is the discovery of gunpowder, usually ascribed to Roger Bacon. Realising the possible uses to which his discovery could be put, Bacon concealed it in cypher, and gunpowder was rediscovered in Germany by Schwarz. Gunpowder, or blackpowder as it is now called, consists of a mixture of potassium nitrate, charcoal and sulphur very intimately ground together. It is readily ignited, even in complete absence of air, and then burns very rapidly. Moreover, if it is burned in a confined space, as in a borehole or a military shell, then as the pressure increases the rate of burning also increases to a high value. If a charge in a borehole is ignited at one end, the flame can propagate at a rate of several hundred metres a second.

Even more rapid reaction can be produced if oxygen and fuel are provided in a single chemical molecule. The discovery of nitroglycerine by Sobrero led to the first product of this type to achieve commercial importance. Nitroglycerine contains enough oxygen to burn all its own

carbon and hydrogen. It is, therefore, capable of an extremely rapid combustion. In practice, however, combustion of this sort is unstable and readily turns into a form of reaction known as detonation. This process of detonation of nitroglycerine can best be regarded, qualitatively, as the passage through the material of a sudden wave of high pressure and temperature which causes the molecules to break down into fragments which later recombine to give the ultimate explosion products. That the process is more vigorous than combustion is shown by the high speed of 8000 m s^{-1} at which it propagates; this speed is also independent of the pressure of surrounding gas. Explosives which detonate like nitroglycerine are known as high explosives.

Nitroglycerine and other high explosives of this type are difficult to initiate into detonation simply by the use of a flame. Mercury fulminate, discovered by Howard, is an explosive of relatively low power which can, however, always be relied on to detonate when ignited by a flame. Explosives like mercury fulminate are known as initiating explosives.

Although many more modern explosives have been added to the few mentioned above, they all belong to one of the three types described, namely,

1. Deflagrating (or propellent) explosives.
2. High explosives (sometimes called secondary explosives).
3. Initiating explosives (sometimes called primary explosives).

In Great Britain, manufacture of gunpowder probably started in the 14th century. By the 16th century there was certainly manufacture at a number of sites, both privately and by the Government. The Royal Gunpowder Factory at Waltham Abbey dates from this period. Gunpowder factories were best placed near forests, to provide charcoal, and near water power, to drive the mills. Kent and the Lake District became important centres. The invention of the safety fuse by Bickford in 1831 led to its manufacture at Tuckingmill in Cornwall.

Guncotton was made at Faversham in 1847, but manufacture ceased after a serious explosion. It was nearly twenty years before manufacture was recommenced, privately at Stowmarket and also at Waltham Abbey. The initial uses were military.

The starting point of the present British commercial explosives industry was the formation of the British Dynamite Company in 1871 by Alfred Nobel and a group of Glasgow business men. Ardeer factory in Ayrshire

was built, and commenced operation in January 1873. Detonators were manufactured from 1877 in a factory at Westquarter in Stirlingshire. TNT was manufactured at Ardeer from 1907. The later history of the company is too complex to be given in detail here. It is sufficient to say that by 1926, as Nobel Industries Ltd., it had acquired many interests other than explosives. In 1926 Nobel Industries Ltd., with Brunner Mond Co., the United Alkali Co., and the British Dyestuffs Corporation, merged to form Imperial Chemical Industries Ltd. At the present time Nobel's Explosives Co. Ltd., a wholly owned subsidiary of I.C.I., has responsibility for the manufacture, distribution and sale of explosives and accessories.

N.E.C. is the major manufacturer with a complete range of explosives and accessories, with factories in Scotland, Wales and England. Explosives and Chemical Products Ltd., with factories in England, is the other manufacturer of explosives for sale. The major commercial manufacturer of ammunition is Imperial Metal Industries (Kynoch) Ltd. at Witton near Birmingham. The British Government has of course a number of Royal Ordnance Factories and establishments to cover all aspects of military explosives.

Explosives of all types are made for commercial and military purposes in many countries throughout the world. It is, however, difficult to obtain any figures which give a worthwhile idea of the magnitude of the explosives industry. Military explosives are usually made under conditions of secrecy and no figures of output are published. Even for commercial explosives published figures are scanty and vary considerably from country to country. Data which are available are given in Table 1.1.

TABLE 1.1	*Annual Production of Commercial Explosives, 1977*

Country	Tonnes per annum
U.S.A.	1 680 000[a]
German Federal Republic	59 000
France	56 000
Spain	43 000
Sweden (1975)	31 000
Greece (1973)	21 000
Italy	16 000
Portugal	5 000

[a] Consumption.

The largest commercial explosives factory in the world is at Modderfontein in South Africa.

The most complete set of statistics is that published in the United States of America, which showed a total consumption of industrial explosives in 1977 of 1 680 000 tonnes. Details of the types of explosives consumed and the industries using the products are given in Tables 1.2 and 1.3 respectively.

TABLE 1.2   *U.S.A. Consumption of Industrial Explosives, 1977*

Type of explosive	Tonnes
Permissibles [a]	22 000
Other high explosives	85 000
Water gels and slurries	144 000
Blasting agents and ANFO	1 432 000
Total	1 683 000

[a] U.S.A. equivalent of British "Permitted"

TABLE 1.3   *U.S.A. Explosives Consumption by Industry, 1977*

Industry	Tonnes
Coal mining	950 000
Metal mining	202 000
Quarrying and non-metal mining	237 000
Construction work	159 000
All other purposes	135 000
Total	1 683 000

No comparable figures are available for Great Britain. Deep coal mines currently record firing 13 million shots per annum using about 8 000 tonnes, but quarrying is certainly a larger user of explosives. A rough guess of the British market for explosives and pyrotechnics could be given as £50 million. There is an appreciable export market; the U.K. Chemical Industry Statistics Handbook gives exports of explosives and pyrotechnics for 1977 as £34·7 million.

The following figures give an indication of British prices. A user of nitroglycerine explosives will pay 55–110p per kg according to type. To

fire a charge of explosive, whatever its size, he will require a plain detonator at 3p (with perhaps 10p worth of safety fuse), an electric detonator at 16p, or a delay detonator at 25p. These are just a few possible figures from a total range of several thousand products!

Although these costs are not high, they do represent a greater expenditure per unit of energy than more conventional means. For example, the following table gives approximate relative costs of energy from explosives and from other well-known sources (neglecting efficiency of use for mechanical purposes).

TABLE 1.4   *Relative Costs of Energy from Various Sources*

Source of energy	Relative cost
Nitroglycerine gelatine explosive	50
Electricity	4
Fuel oil	1

The particular advantage of explosives is the rapid generation of energy. Thus a single cartridge of blasting gelatine 3 cm in diameter produces on detonation about 60 000 MW—appreciably more than the total electric power station capacity of the United Kingdom.

Explosives are used mainly for doing mechanical work and particularly for breaking rock and coal. The advantages in cost of electrical and similar forms of energy mean that there is a continued incentive for users to replace explosives by mechanical methods of working. This is particularly noticeable in the coal industry, where mechanical operation offers other advantages at the same time. The amount of explosive used per ton of coal is therefore diminishing, and with production of coal in Great Britain remaining static, coal mining explosives are in smaller demand now than in previous years. Throughout the world, also, the conventional explosives industry is suffering from increasing competition from cheap mixtures of ammonium nitrate and oil which can be made to detonate and which in some countries may be mixed by the user on the site of operation. Such mixtures have replaced conventional explosives on many sites, particularly in North America. A qualitative picture of the trend of the explosives industry is given in Fig. 1.1, from which it will be seen that the total usage has increased (although the rate has been less than the general

expansion of the world economy). Conventional explosives, on the other hand, have passed through a peak and the industry is operating at a lower level than previously. There are signs that this level is now being kept steady. World usage of detonators and other accessories is thought to have shown a general increase over the years.
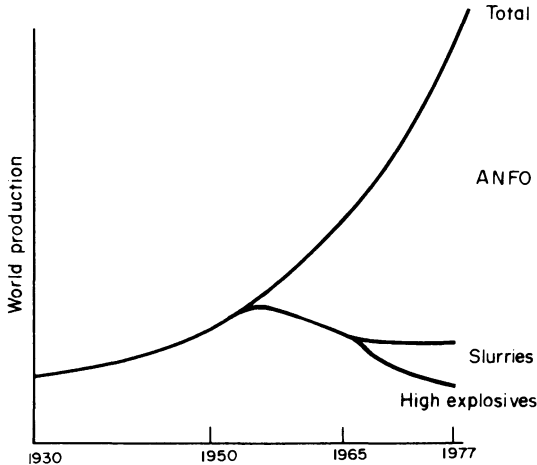

FIG. 1.1. Trend of world production of commercial explosives.

In all countries the manufacture, transport and sale of explosives are strictly controlled by law. The nature of the regulations does, however, vary considerably throughout the world. In Communist countries, commercial and military explosives are made in the same factories and under precisely the same conditions by the State. In the rest of the world, manufacture of commercial explosives is mainly by private firms, as is indeed the case in Britain. The operations of these firms is however closely controlled by the Government, whilst conditions of transport are increasingly becoming matters of international concern. In the U.S.A., manufacture is again by private companies, but the conditions are laid down by the individual states and only inter-state transport is regulated by the Federal Government. In almost all countries, governments maintain their own research and testing facilities, and in most countries private industry also carries out research and development work on explosives.

In Great Britain manufacture, storage and transport of industrial

explosives are governed not only by the general provisions of the Health and Safety at Work Act but more specifically by the Explosives Acts of 1865 and 1923. There are also numerous Statutory Instruments made under the 1865 Act. Administration of these regulations is by H.M. Inspectors of Explosives who form part of the Health and Safety Executive. However the control of Government Establishments and the transport of military explosives is the responsibility of the Ministry concerned.

A licence is needed for making explosives on any scale other than small amounts for chemical experiment and so it is illegal to manufacture explosives or make rockets for private use. An intending manufacturer must supply drawings of the proposed factory and have these agreed by the local authorities. They are then submitted to the Inspectors of Explosives who will, when satisfied, issue the factory licence and indicate the working regulations to be observed. Requirements which must be satisfied relate to the construction of the buildings and their surrounding protective mounds and their distances from other buildings, public highways etc., as laid down in the table of safety distances approved under the Act. The factory will be authorised to make explosives in a Schedule according to Definitions which must be agreed by H.M. Inspectors of Explosives. Should a new explosive be considered for manufacture, then an Authorised Definition must be approved beforehand. Such approvals are based on tests essentially of stability and safety in handling.

Special authorisations are available for manufacture at the site of use of ammonium nitrate/fuel oil and certain slurry explosives provided that the equipment used and its position on the site are suitable.

The Explosives Acts and Orders made under them also stipulate how explosives may be packed for storage and transport. Blasting explosives are packed in an inner wrapper which prevents spillage and gives protection against moisture and then in an outer wrapper which provides strength in handling. In general the outer case is nowadays of fibreboard, but wooden cases are still used in some parts of the world.

The transport of explosives is covered strictly by regulation and this is becoming increasingly international in character. A committee of the United Nations Organisation has produced an improved classification of explosives and specified agreed methods of packing suited to each item. These proposals now form the basis of the conditions of transport by air

laid down by IATA (International Air Transport Association) for the limited range of explosives which may be carried on aircraft. The same proposals are used for transport by sea as laid down by IMCO (Intergovernmental Maritime Consultative Organisation) and the British "Blue Book" has been adapted to correspond. It is hoped that these leads will be followed in the near future by the international bodies concerned with transport by road, rail and inland waters. Meantime, in Britain, road transport of more than 50 kg of blasting explosive requires specially designed vehicles which may carry up to a maximum of 4 tonnes. In rail transport suitable wagons are required and the load must not exceed 20 tonnes.

Regulations concerning the manufacture and use of explosives appear complicated, but their necessity is obvious. Experience and goodwill are however always essential to ensure the smooth running of the system and thus public safety.

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Part I. High Explosives

CHAPTER 2

General Principles

History

The first explosive used was not a high explosive but gunpowder, discovered in the 13th century and rediscovered in the 14th century. It was used for military purposes from the 14th century onwards, and first introduced into blasting practice in Hungary in the 17th century. It soon spread to Germany and to Britain. Gunpowder, as noted above, is a deflagrating explosive and has long been overshadowed in importance by high explosives.

The first high explosive discovered was probably nitrocellulose, in the period 1833 to 1846, but its development was long delayed by difficulties in obtaining a stable product. The two major discoveries in this field were of nitroglycerine by Sobrero in 1847 and TNT by Wilbrand in 1863. Of these, the first to attain commercial importance was nitroglycerine.

Sobrero early recognised the dangers of handling nitroglycerine and it was only the tenacity of Alfred Nobel which finally succeeded in making nitroglycerine a commercially useful material. Alfred Nobel followed his father's interest in explosives and in spite of a number of explosions and accidents, including one which killed his younger brother and indirectly his father, he devised in a laboratory on a barge a safe method of producing nitroglycerine. Equally important, he realised that nitroglycerine, unlike gunpowder, could not be set off by flame, but needed a shock to cause effective initiation. He therefore invented first his patent detonator incorporating gunpowder, and then finally the modern detonator containing mercury fulminate. This he introduced in 1865. He realised, also, the hazards involved in handling liquid nitroglycerine and invented first guhr dynamite using kieselguhr (diatomaceous earth), and second blasting gelatine, both of which are safe and highly powerful detonating

explosives. He early realised, and acquired patents for, the inclusion in explosives of oxidising salts such as nitrates together with combustibles. By 1875 Nobel had completed the invention of ordinary blasting explosives which were to dominate the field well into the 20th century. Nobel was a prolific inventor and a man whose life story makes fascinating reading.

From the days of Nobel to about 1950 the scientific basis of commercial explosives remained relatively unchanged, although continuous and numerous improvements in manufacturing methods occurred throughout the world. There were, however, many advances in military explosives, note of which will be made later. These advances were, of course, largely due to the two world wars, which occurred since the death of Alfred Nobel. There were also many advances in the development of permitted explosives designed for use in gassy coal mines.

In the 1950's a sudden and dramatic change affected the explosives industry in many parts of the world. This was the introduction in the U.S.A., Sweden and Canada of ammonium nitrate sensitised with fuel oil as a major blasting explosive. A slower but also important change started in the 1960's with the development of slurry explosives in the U.S.A., Canada and other countries.

The Nature of Detonation

The process of detonation in an explosive, the blasting effects of such an explosive in coal or rock, and the destructive effects of military high explosives all depend on the operation of shock waves. It is, therefore, intended to give here an elementary account of shock waves in inert media and in explosives before discussing individual high explosives.

A compression wave of low intensity is well known in ordinary sound waves in the air, or in other media. Sound is propagated with a velocity determined by the following equation:

$$c^2 = \frac{\partial p}{\partial \rho}\bigg|S \qquad (1)$$

where c is the velocity of the sound wave, p is the pressure, ρ is the density and S is the entropy (which remains constant). Qualitatively it is

convenient to remember that the velocity of sound increases as the compressibility of the medium decreases.

In the case of sound waves, which are of very low intensity, the pressure and density of the medium remain effectively constant throughout the process. Therefore, all parts of a sound wave are transmitted at the same velocity, so that a sinusoidal (sine) wave, for example, remains sinusoidal indefinitely during propagation.

With shock waves it can no longer be assumed that pressure and density remain constant. Indeed, at the peak of a strong shock wave the pressure can be many thousands of atmospheres and the density appreciably increased. Under such conditions the velocity no longer is that of a sound wave. In practice, as pressure or density is increased, the compressibility decreases so that the velocity of propagation of the disturbance increases. If we can imagine an intense sinusoidal half-wave generated in a medium, then the velocity of propagation of the peak of the wave where the material is at high density would be greater than the velocity of the front of the wave where the material is almost at its original condition. Therefore, the peak would overtake the front and the shape of the wave would alter as shown in Fig. 2.1, until ultimately the wave form becomes a sudden and discontinuous jump to a high pressure followed by a gradual fall. This is the typical and inevitable profile of a shock wave in an inert medium. As transmission continues, however, losses gradually reduce the peak pressure until ultimately the shock wave degenerates into an ordinary sound wave.
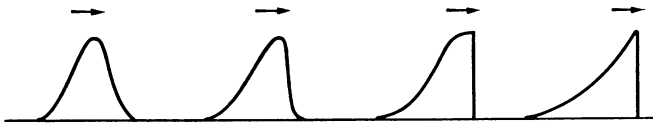
Fig. 2.1. Development of a shock wave.

Shock waves, like all other waves, undergo the normal processes of reflection and refraction in passing from one medium to another. The case of reflection is of particular importance. Three possibilities are shown in Figs. 2.2(a), 2.2(b) and 2.2(c). Figure 2.2(a) shows the position where a shock wave in a non-compressible (dense) medium meets a boundary with a highly compressible (light) medium. The shock wave is reflected at the
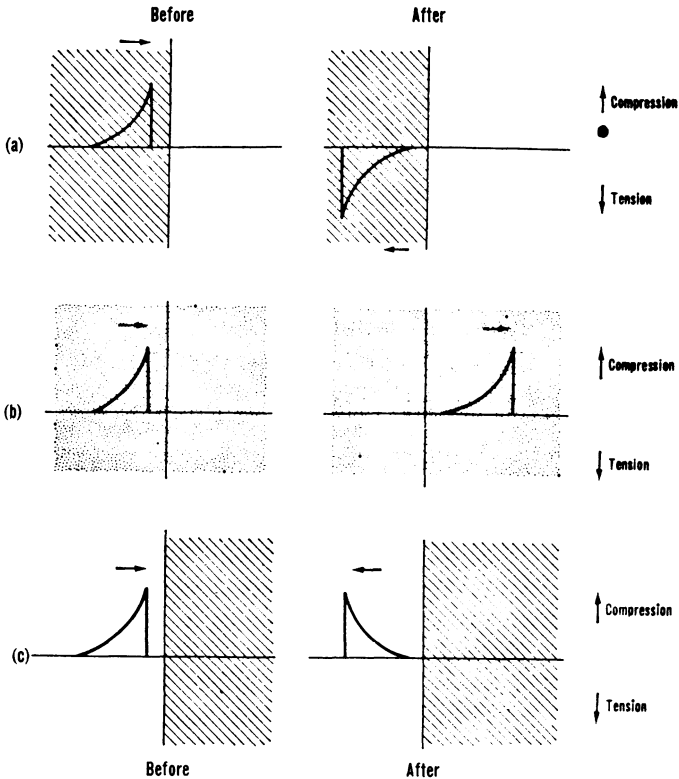
FIG. 2.2. Reflection of shock waves. (a) Shock wave in denser medium.
(b) Matched media. (c) Shock wave in lighter medium.

interface as a rarefaction wave, provided that the tensile strength of the medium makes this possible. Figure 2.2(c) shows the extreme contrast to this where a wave in a compressible medium meets a medium of low compressibility. In this case again the wave is reflected, but as a compression wave rather than a rarefaction wave. Case 2.2(b) is the intermediate case where the media have similar compressibility and in this case, and this case alone, is the shock wave transmitted across the boundary without alteration.

A shock wave in an inert medium is not propagated indefinitely without

change because rarefaction waves can always overtake the pressure wave and reduce the peak pressure until the conditions of a sound wave are reached. For a stable shock wave to be maintained, a source of energy must be available which will enable the wave to be propagated without rarefaction waves occurring. This is what happens when detonation occurs in an explosive.

When a detonation wave passes through an explosive, the first effect is compression of the explosive to a high density. This is the shock wave itself. Then reaction occurs and the explosive is changed into gaseous products at high temperature. These reaction products act as a continuously generated piston which enables the shock wave to be propagated at a constant velocity. The probable structure of the detonation zone is illustrated in Fig. 2.3.
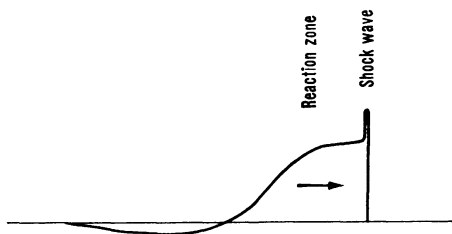
FIG. 2.3. Structure of detonation wave.

Mathematically, the following three equations can be written down representing respectively the application of the laws of conservation of mass, momentum and energy.

Mass:
$$\frac{D}{v_1} = \frac{D - W_2}{v_2} \qquad (2)$$

Momentum:
$$\frac{D^2}{v_1} + p_1 = \frac{(D - W_2)^2}{v_2} + p_2 \qquad (3)$$

Energy:
$$E_1 + D^2 + p_1 v_1 = E_2 + \tfrac{1}{2}(D - W_2)^2 + p_2 v_2 \qquad (4)$$

where D = velocity of detonation,

W_2 = velocity of material behind the wave, relative to that in front,

v = specific volume,

p = pressure,

E = specific internal energy,

and subscripts 1 and 2 relate to the initial and final states of the explosive respectively.

It will be noted that E_1 is the specific internal energy of the unreacted explosive, whereas E_2 is the specific internal energy of the explosion products at pressure p_2 and specific volume v_2. These equations are deduced from physical laws only and are independent of the nature or course of the chemical reaction involved.

Equations (2) and (3) can be solved to give the following equations for D and for W_2:

$$D = v_1 \sqrt{[(p_2 - p_1)/(v_1 - v_2)]} \tag{5}$$

$$W_2 = (v_1 - v_2)\sqrt{[(p_2 - p_1)/(v_1 - v_2)]} \tag{6}$$

It will be noted that as p_2 is greater than p_1, v_2 must be less than v_1, and W_2 (known as the streaming velocity) is positive, meaning that the explosion products travel in the same direction as the detonation wave. This positive streaming velocity is a characteristic and identifying property of a detonation wave.

These are the basic equations of the hydrodynamic theory of detonation. If p_2 and v_2 can be determined, they enable the remaining features of the detonation wave to be calculated. Unfortunately p_2 and v_2 relate to conditions in the detonation wave and not to the lower pressure conditions which the explosion products would reach at equilibrium in, for example, a closed vessel. Therefore, further calculations are needed to determine p_2 and v_2.

In studying detonation, it is convenient to use diagrams of the type illustrated in Fig. 2.4. In these, the pressure is plotted over the specific volume. The original explosive corresponds to point A. The reaction products are represented by the curve BC, known as the Rankine–
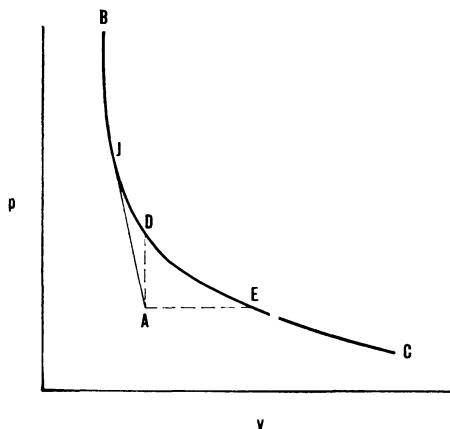
FIG. 2.4. Rankine–Hugoniot diagram.

Hugoniot curve, which represents all possible points in the area which satisfy the chemical equilibria and entropy conditions of the explosive reaction products. It is a locus which is defined by, and can be calculated from, the energy equation — equation (4). (p_2, v_2) must therefore be a point on this line. As noted above, v_2 must be less than v_1, so the point must lie on the part of the curve BD. To determine exactly where the point (p_2, v_2) lies in the curve BD requires difficult arguments which are not reproduced here, but which show that the point can be obtained by drawing a tangent from A to the curve; this is known as the Chapman–Jouguet condition, and the tangent is the Raleigh line. Thus the point J shown in Fig. 2.4 gives p_2 and v_2. Substituting these values in equation (5) gives the calculated detonation velocity.

The major difficulty in applying this hydrodynamic theory of detonation to practical cases lies in the calculation of E_2, the specific internal energy of the explosion products immediately behind the detonation front, without which the Rankine–Hugoniot curve cannot be drawn. The calculations require a knowledge of the equation of state of the detonation products and also a full knowledge of the chemical equilibria involved, both at very high temperatures and pressures. The first equation of state used was the Abel equation

$$p_2(v_2 - a) = n_2 R T_2 \tag{7}$$

where a is a constant, n_2 is the number of gramme-molecules of gas, and R is the gas constant, but this becomes inaccurate for explosives with a density above $0 \cdot 1$ g ml^{-1}. Probably the most successful equation so far used is that by Paterson and is a virial type equation as follows

$$p_2 = n_2 RT(1 + b\rho + 0 \cdot 625b^2 \rho^2 + 0 \cdot 287b^3 \rho^3 + 0 \cdot 193b^4 \rho^4) \qquad (8)$$

where b is a constant.

Typical results are given in Table 2.1 for pure explosives which give only gaseous products.

A semi-empirical equation was introduced by Kistiakowsky and Wilson and took the following form:

$$p_2 v_2 = n_2 RT(1 - xe^{\beta x}) \quad \text{where} \quad x = \rho k T^{-\alpha}$$

TABLE 2.1   *Calculated Properties of Explosive Compounds*

Compound	Density	Energy	Streaming velocity	Velocity of detonation (m s^{-1})	
	(g ml^{-1})	(J g^{-1})	(m s^{-1})	Calculated	Observed
Nitroglycerine	1·60	6283	1550	8060	8000
PETN	1·50	5881	1550	8150	7600
Tetryl	1·50	5810	1320	7550	7300
TNT	1·50	5413	1140	6480	6700
Nitroguanidine	0·60	2658	1027	4040	3850
Ammonium nitrate	1·00	1580	832	3460	—

The constants α and β were first chosen to give the best fit to experimental detonation velocity measurements for a wide variety of materials. They have more recently been revised by Cowan and Fickett to give better agreement with experimentally measured detonation pressures. For numerous other approaches to the problem of the equation of state under detonation conditions, readers are referred to the book by Cook and a paper by Jacobs.

Commercial explosives frequently contain salts, or give other solid residues. In calculations these cause difficulties, as it is not certain whether solid ingredients reach equilibrium with the explosion products. In the calculations it is possible either to assume thermal equilibrium, or to

assume no heat transfer to the solids. In Table 2.2 are given the results by Paterson of calculations on a number of commercial explosives, when necessary according to each method.

TABLE 2.2   *Calculated Properties of Commercial Explosives*

Explosive type	Energy	Streaming Velocity	Velocity of detonation (m s^{-1})	
	(J g^{-1})	(m s^{-1})	Calculated	Maximum observed
Blasting gelatine	6584	1540	7900	7800
Gelatine	5559	1290	6520	6600
Ammon gelignite	4218	1220	6310	6000
Permitted gelignite (P1)	3277	1065^a	5850^a	5800
		900^b	5040^b	
Nitroglycerine powder	3737	1090	4270	—
Permitted powder (P3)	2132	830^a	3490^a	3000
		730^b	3060^b	
TNT powder	3984	1172	5060	5250

^{a} Salt remaining cold.
^{b} Salt in thermal equilibrium.

Tables 2.1 and 2.2 show that theory enables detonation velocities to be calculated in close agreement with those observed experimentally. This, unfortunately, is not a critical test of the theory as velocities when calculated are rather insensitive to the nature of the equation of state used. A better test would be to calculate the peak pressures, densities and temperatures encountered in detonation, and compare these with experimental results. The major difficulties here are experimental. Attempts to measure temperatures in the detonation zone have not been very successful, but better results have been obtained in the measurement of densities and pressures. Schall introduced density measurement by very short X-ray flash radiography and showed that TNT at an initial density of 1·50 increased 22% in density in the detonation wave. More recently detonation pressures have been measured by Duff and Houston using a method (introduced by Goranson) in which the pressure is deduced from the velocity imparted to a metal plate placed at the end of the column of explosive. Using this method, for example, Deal obtains the detonation pressures for some military explosives recorded in Table 2.3. More

TABLE 2.3   *Detonation Pressures of Military Explosives*

Explosive	Density (g ml⁻¹)	Detonation velocity (m s⁻¹)	Streaming velocity (m s⁻¹)	Detonation pressure (10^8 Pa)
RDX	1·767	8639	2213	337·9
TNT	1·637	6942	1664	189·1
RDX/TNT (77/23)	1·743	8252	2173	312·5

recently Paterson has measured detonation pressures of some commercial explosives using a similar method with the results given in Table 2.4. Comparison of these measured pressures with those calculated by the hydrodynamic theory show that so far only equations of state containing empirical constants give satisfactory agreement.

TABLE 2.4   *Detonation Pressures of Commercial Explosives*
(3·18 cm diam.)

Explosive		Detonation pressure (10^8 Pa)
Name	Type	
Polar blasting gelatine	Gelatine	160 (high velocity) 19 (low velocity)
Belex	Semi-gelatine	31
Polar Ajax	P1 gelatine	13
Unigel	P3 gelatine	9
Polar Viking	P1 powder	12
Unifrax	P3 powder	6
Carribel	P4 powder	5
ANFO (2% oil, 5·08 cm diam.)		11

The simple theory outlined here can apply only to charges which are infinite in size, or which are so large that lateral losses in the reaction zone are negligible. In many practical cases the cartridge diameter is no longer sufficiently large in comparison with the thickness of the reaction zone for this assumption to be true and lateral losses lead to observation of reduced detonation velocities. With many explosives, if the diameter is decreased below a certain critical diameter, losses are so great that detonation no longer can occur. Typical examples of the variation of observed detonation velocity with cartridge diameter are given in Table 2.5.

TABLE 2.5   *Variation of Velocity of Detonation with Cartridge Diameter*

Diameter (cm)	Velocity of detonation (m s^{-1})	
	TNT powder	Nitroglycerine powder
1·9	3190	1830
3·2	3680	2250
5·1	4060	2610
6·4	4030	—
7·6	4100	3150
10·2	4560	3290
12·7	—	3440
15·2	4815	—
21·6	—	3920

Extension of the hydrodynamic theory to explain the variation of detonation velocity with cartridge diameter takes place in two stages. First, the structure of the reaction zone is studied to allow for the fact that the chemical reaction takes place in a finite time: secondly, the effect of lateral losses on these reactions is studied. A simplified case neglecting the effects of heat conduction or diffusion and of viscosity is shown in Fig. 2.5. The Rankine–Hugoniot curves for the unreacted explosive and for the detonation products are shown, together with the Raleigh line. In the reaction zone the explosive is suddenly compressed from its initial state at
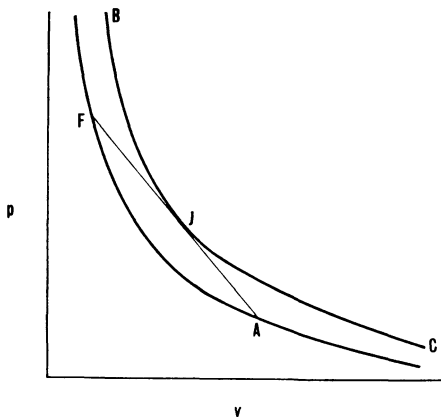

FIG. 2.5. Rankine–Hugoniot diagram for detonation.

point *A* to a state at point *F*. Reaction then occurs with the pressure falling along the line *FJ* until at the end of the reaction zone a point *J* is reached and stable detonation conditions arrived at. The actual shape of the pressure wave is shown in Fig. 2.6 where the so-called Neumann peak of twice the detonation pressure is shown. A more complete solution by Hirschfelder and Curtiss shows that the effects of viscosity and thermal transfer by diffusion and conduction are to reduce the magnitude of the Neumann peak and the steepness of the initial increase in pressure. One such solution is sketched in Fig. 2.6 where a first order chemical reaction has been assumed. The shape will depend, however, on the magnitude of the heat losses and in some cases the initial peak need not occur at all. Some evidence for the existence of the Neumann peak has been obtained as, for example, by Duff and Houston. In their measurements the peak pressure reached was 42% above p_2.
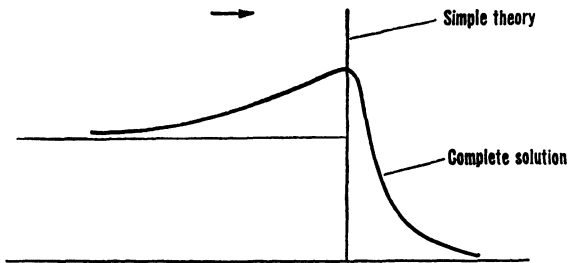

FIG. 2.6. Calculated shape of detonation wave head.

Cook has propounded a rather different theory of the nature of the reaction zone. He emphasises that the demonstrable electrical conductivity of the detonation wave is evidence of a high thermal conductivity. Both these effects are ascribed to ionisation of the explosion products. In terms of the reaction zone, this implies a steady pressure with no peaks.

Theoretical considerations of charges of limited diameter have taken one of two forms. The former assumes that the effects are best described as a result of the curvature of the wave front in the explosive (this can be demonstrated experimentally), or of reduction of the driving pressure by lateral expansion. Solutions of this type have been given by Eyring and co-workers and by Jones. Alternatively, the variation in velocity of

detonation can be explained as a result of incomplete reaction during the actual detonation wave. Explanations of this type have been put forward by Cook and also by Hino. The following equations illustrate the dependence of detonation velocity on charge diameter according to the various theories.

Eyring, Powell, Duffey and Parlin:

$$D/D_0 = 1 - z/d \quad \text{for } z/d < 0.25$$

Jones (cf. Jacobs):

$$(D/D_0)^2 = 1 - 3.2 \, (z/d)^2$$

Cook:

$$(D/D_0)^2 = 1 - (1 - \frac{4ad'}{3tD})^3$$

where d = diameter of charge,
z = reaction zone thickness,
a = constant,
$d' = d - 0.6$ cm,
t = reaction time.

The thickness of the reaction zone in high explosives is usually in the range 1–10 mm.

Liquid nitroglycerine and gelatinous explosives made from it can exhibit two stable velocities of detonation, of approximately 2000 and 8000 m s^{-1} respectively. The phenomenon is complicated by the occurrence of air bubbles in such explosives and has not yet been completely explained.

The theory of detonation has also been extended to study the process of initiation of reaction by the commonest means used in practice, namely, by the shock wave arising from another high explosive. Campbell, Davis and Travis have studied the initiation by plane shock waves of homogeneous explosives, particularly nitromethane. Initiation occurs at the boundary of the explosive after an induction period which is of the order of a microsecond and which depends markedly on initial temperature. During the induction period the shock wave has proceeded through the explosive and compressed it. The detonation initially in compressed explosive has a velocity some 10% above normal, but the detonation soon overtakes the

shock front and the detonation velocity falls abruptly to the normal value. The process is shown in Fig. 2.7(a). These results can be explained adequately on the basis of thermal explosion theory as developed, for example, by Hubbard and Johnson.
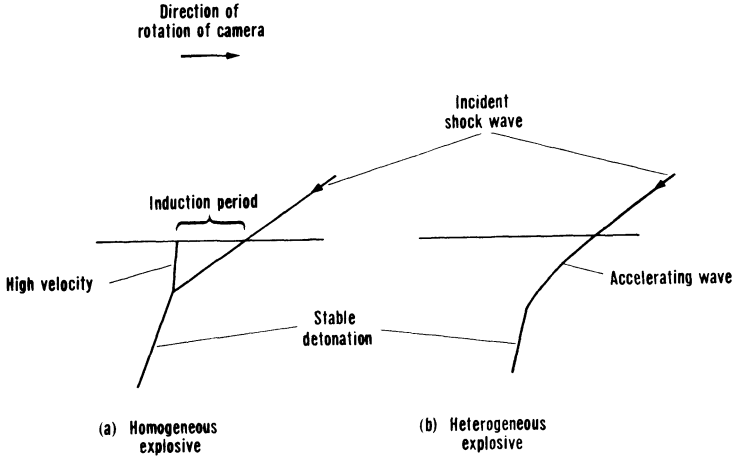

FIG. 2.7. Initiation of detonation in explosives, as shown in a rotating mirror camera.

Even slight lack of homogeneity in explosives or shock wave form leads to an alternative mode of initiation characteristic of ordinary military or commercial explosives in solid or gelatinous form. This process has been studied by Campbell, Davis, Ramsay and Travis and is depicted in Fig. 2.7(b). The shock wave first proceeds through the explosive with slow acceleration. After a few centimetres there is abrupt transition to detonation at normal velocity. The distance at which transition occurs is independent of temperature but can be reduced by (i) increasing the pressure of initiating shock, (ii) increasing the fineness of the active ingredients, or (iii) for powder explosives reducing the loading density. Deliberate introduction of centres of heterogeneity, such as air bubbles or barium sulphate, is well known to reduce the distance. These results cannot be explained by general thermal explosion as there is insufficient energy to give the required temperature rise. They can be explained on the basis of reaction at local centres or "hot spots".

A similar explanation had already been given for the initiation of explosives by impact and friction. These phenomena have been extensively studied, particularly by Bowden and his school. Their work demonstrated two particularly important modes of initiation:

1. By adiabatic compression of gas. This is particularly noticeable in liquid explosives such as nitroglycerine, where even the moderate compression of small gas bubbles can readily lead to initiation of the explosive.

2. By the development of hot spots by friction. This is shown particularly by the effect of added materials of a gritty nature. For initiation to occur, the melting point of the grit must be above a limiting temperature dependent on the explosive. Initiation is favoured by a low thermal conductivity and also by a high hardness value.

Burning of high explosives can on occasion lead to detonation, particularly if large quantities are involved. In close bomb tests Wachtell, McKnight and Shulman find a reproducible pressure above which burning becomes progressively faster than would be expected from strand burner tests (see p. 179). For TNT this pressure is about 45 MPa, but for propellants much higher. They regard this characteristic pressure as a measure of the liability to detonation.

The external effects of a detonating explosive are of two types, due in the first place to the shock wave and in the second place to the expansion of the detonation products. The detonation wave reaching the end of a cartridge is propagated into the further medium, whether this be air, rock, or water. Because of the positive streaming velocity of the detonation wave, the effects are particularly strong at the terminal end of the cartridge. Although a cartridge detonated in air can produce a shock wave with a velocity even higher than that of the explosive itself, the energy in this wave is relatively small. If the explosive completely fills a metal case, or a borehole in rock, much greater amounts of energy can penetrate into the surrounding media. In either case, however, by far the greater proportion of the energy of the explosive is liberated during the expansion of the gaseous products and it is in general this work of expansion which causes the explosive to have its desired effect. The amount of energy available from an explosive for this purpose can be calculated by integrating the mechanical work done during the expansion of the products to

atmospheric pressure. More often, however, it is measured by some practical test (cf. Chapter 6).

A special simple case of work done by an explosive is observed when charges are fired under water. The observed effects are first a shock wave which is transmitted through the water, secondly an expanding bubble of gas. This bubble expands to a maximum size and then collapses, to expand again and vibrate until the energy has been dissipated. Rather more than half the energy remaining available in the gas is transmitted through the water during each expansion of the bubble. These phenomena are described in detail by Cole.

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Military High Explosives

FOR military purposes high explosives are used as filling for shell, bombs and warheads of rockets. The basic requirements for such explosives are the following:

1. Maximum power per unit volume.

2. Minimum weight per unit of power.

3. High velocity of detonation.

4. Long-term stability under adverse storage conditions.

5. Insensitivity to shock on firing and impact.

Requirements 1 and 3 follow immediately from the considerations of the theory of detonation when it is remembered that the purpose of the charge is to obtain maximum effect, both from the shock wave of the explosive and also from the destructive effect of expansion of the explosion products. Requirements 1 and 2 follow from the consideration that any reduction in size and weight of the warhead of a missile, or in a shell, immediately makes it possible to increase the range and therefore the usefulness of the weapon. Requirement 5 relates not only to safety, but also the desirability, particularly for armour-piercing ammunition, for the time of detonation to be determined solely by the functioning of an appropriate fuze.

In this chapter the explosives employed are discussed; their actual application is described in Part III. The most important properties of the commonest military explosives are listed in Table 3.1.
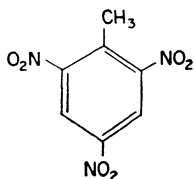
TABLE 3.1 *Properties of Military Explosives*

Explosive	m.p. (°C)	Density (g ml^{-1})	Weight strength % Blasting gelatine[a]	Maximum detonation velocity (m s^{-1})
TNT	80·7	1·63	67	6950
PETN	141·3	1·77	97	8300
RDX	204	1·73	100	8500
Tetryl	129	1·6	84	7500

[a] See p. 62.

TRINITROTOLUENE

Trinitrotoluene is the 2, 4, 6-isomer of the following constitution:

The starting material is pure toluene, specially free from unsaturated aliphatic hydrocarbons. This is nitrated in several stages to avoid oxidation side reactions which occur when toluene itself is mixed with strong nitrating acids. The traditional process employed three nitrating stages; as an example the nitrating acids used in France are given in Table 3.2.

TABLE 3.2 *French Nitrating Acids for TNT Manufacture*

	1st stage	2nd stage	3rd stage
Nitric acid wt. %	28	32	49
Sulphuric acid wt. %	56	61	49
Water wt. %	16	7	2

During and since the Second World War, the three-stage process has been replaced by continuous methods of nitration employing a larger number of stages. In these, the chemical engineering can differ widely, but in principle toluene enters the process at one end and trinitrotoluene is

produced at the other. The nitrating acid flows in the opposite direction, being fortified as required at various points. One of the most important factors is stirring in the nitrators, as this markedly affects the speed and completeness of nitration, particularly in the later stages. For a discussion of these methods the reader is referred to a book by Urbanski.

The crude product contains isomers other than that required and also nitrated phenolic compounds resulting from side reactions. The usual method of purification is to treat the crude product with sodium sulphite, which converts asymmetric trinitro compounds to sulphonic acid derivatives, and to wash out the resulting soluble products with alkaline water. The purity of the product is determined by the melting point, the minimum value for Grade I TNT commonly being 80·2°C. Unless adequate purity is achieved, slow exudation of impurities can occur during storage and the TNT then becomes insensitive.

TNT is relatively safe to handle and of low toxicity. It is, therefore, preferred to picric acid and ammonium picrate which give sensitive compounds with a variety of metals, and to trinitrobenzene or hexanitrodiphenylamine which are highly toxic.

TNT contains insufficient oxygen to give complete combustion of the carbon on detonation. It can, therefore, usefully be mixed with ammonium nitrate, which has an excess of oxygen. The resulting explosives, known as amatols, are more powerful and cheaper than TNT itself, but in general have a lower velocity of detonation. A proportion of 60% ammonium nitrate is perhaps the commonest of these compositions.

PENTAERYTHRITOL TETRANITRATE
(PETN, PENTHRITE)

This material has the following formula:
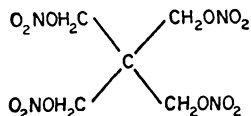
Pentaerythritol is made commercially by the reaction of formaldehyde and acetaldehyde in the presence of alkali. It can be nitrated by adding it to strong nitric acid at temperatures below about 30°C. An excess of nitric

acid is used so that the refuse acid from the reaction contains at least 75% nitric acid, as refuse acids of lower strength can be unstable. The washed product is reprecipitated from acetone to give a suitable crystal size and adequate stability on storage. PETN is always transported wet with water, and dried only as required.

PETN, discovered in 1895, is a solid melting at 141°C and is a very powerful explosive. It is very stable both chemically and thermally.

Pure PETN is too sensitive to friction and impact for direct application for military purposes. It can usefully be mixed with plasticised nitrocellulose, or with synthetic rubbers to obtain plastic or mouldable explosives. The commonest application, however, is in conjunction with TNT in the form of pentolites. Pentolites are usually obtained by incorporating PETN into molten TNT. A small amount of the PETN goes into solution, but the bulk remains suspended in the liquid and the whole mix can suitably be used in preparing cast charges. Pentolites containing 20–50% PETN are the commonest in practice.

RDX (CYCLOTRIMETHYLENE-TRINITRAMINE, CTMTN, CYCLONITE, HEXOGEN)

RDX has the following formula:
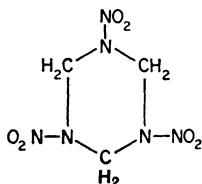
It is made by the nitration of hexamine (hexamethylenetetramine), itself prepared from formaldehyde and ammonia. Hexamine was originally nitrated with a large excess of concentrated nitric acid at temperatures below 30°C and the product recovered by adding the reaction liquor to an excess of chilled water. Later the yield was improved by adding ammonium nitrate to the reaction as this reacts with the liberated formaldehyde. A much-used process converts the hexamine first to its dinitrate, which is then reacted with ammonium nitrate, nitric acid and acetic anhydride (the last reagent being re-formed from the product by use
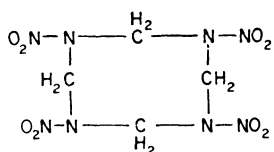
of ketene). The RDX can be isolated by evaporation of the mother liquor, and then purified by washing.

RDX is a white solid melting at 204°C. Originally discovered by Henning in 1899, it attained military importance during the Second World War owing to its lower sensitiveness than PETN. It is very stable, both chemically and thermally.

RDX may be used alone in pressed charges, although for this purpose tetryl is a more general choice. For shell and bomb fillings it is too sensitive alone to initiation by impact and friction and is either desensitised with wax, or else used like PETN in admixture with TNT. RDX may also be compounded with mineral jelly and similar materials to give a useful plastic explosive.

Nitration of hexamine dinitrate in the presence of acetic anhydride can also give another explosive of high power and high stability called HMX (tetramethylenetetranitramine). This has the following structure:

$$O_2N-N \underset{\substack{|\\H_2C}}{\overset{\substack{H_2\\C}}{\rule{2cm}{0pt}}} N-NO_2$$

$$O_2N-N \underset{H_2}{\rule{2cm}{0pt}} C \rule{1cm}{0pt} N-NO_2$$

TETRYL (CE, 2, 4, 6-TRINITROPHENYLMETHYLNITRAMINE)

Tetryl has the following formula:
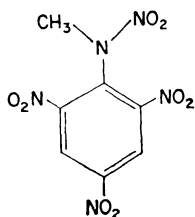
It was discovered by Michler and Meyer in 1879 and was made by the nitration of dimethylaniline. One methyl group is oxidised and at the same time the benzene nucleus is nitrated in the 2, 4, 6-positions. The usual method of preparation from dimethylaniline is to dissolve 1 part of dimethylaniline in 14 to 15 parts of sulphuric acid; to this solution about 9 parts are added of a mixed acid containing 67% of nitric acid and 16% of

sulphuric acid. The nitration is carried out at about 70°C. The water content of the mixture must be kept reasonably low or benzene insoluble impurities of benzidine derivatives are produced.

More recently methylamine is treated with 2, 4- or 2, 6-dinitrochlorobenzene (usually in the form of an unseparated mixture of isomers) to give dinitrophenylmethylamine. This without separation is then nitrated to tetryl.

In either case purification is carried out by washing in cold water and boiling water, the latter hydrolysing tetra-nitro compounds. Finally, the tetryl is recrystallised by solution in acetone and precipitation by water, or recrystallised from benzene.

Tetryl is a pale yellow solid, melting at 129°C. It is moderately sensitive to initiation by friction or percussion. Tetryl is most used in the form of pressed pellets as primers for other less easily initiated explosives.

Other Military Explosives

The explosives described above offer a selection of powerful and thermally stable explosives suitable for use for military purposes. The search for even stronger and more satisfactory explosives always continues. Objects of present research are in general to give compounds which are more stable at high temperatures and which, if possible, have higher strength. Many such compounds have been described, but apparently none have come into any extensive use. Mention may, however, be made of an explosive described by DuPont which has the remarkable thermal stability of withstanding heating to 350°C. This has the following structure:
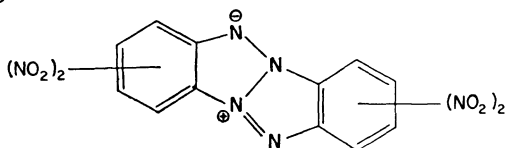
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Manufacture of Commercial Explosives

Ammonium Nitrate

Ammonium nitrate is the cheapest source of oxygen available for commercial explosives at the present time. It is used by itself in conjunction with fuels, or to give more sensitive explosives in admixture with solid fuels and sensitisers such as nitroglycerine and TNT. It is, therefore, a compound of particular importance for the explosives industry.

Ammonium nitrate is made by the neutralisation of nitric acid with ammonia. The details of these processes are given in other volumes of this series. For particular application in explosives, ammonium nitrate is required in specialised forms, of which the following two are the most important.

For use in explosives sensitised by high explosive ingredients, ammonium nitrate should be of a dense and non-absorbent character. Whilst absorbent ammonium nitrate can be employed, it tends to be of lower density and therefore gives lower bulk strengths to the final explosive; it also absorbs a larger amount of nitroglycerine and requires more of this expensive ingredient to give a suitable gelatinous consistency. Dense ammonium nitrate is made either by crystallisation from solution, followed, if necessary, by grinding and screening, or more generally by spraying a melt containing at least 99·6% of ammonium nitrate down a short tower. The spray process produces spherical particles which can be taken from the bottom of the tower and cooled with the minimum of drying. For many years setting of ammonium nitrate, due to absorption of moisture and subsequent temperature change or drying out, led to caking of the salt and corresponding difficulties in handling. Nowadays this is overcome by adding either crystal habit modifiers which cause

recrystallised ammonium nitrate to have low physical strength, or else by other additives which appear to lubricate the surface of the crystals. In this way, provided storage conditions are reasonable, ammonium nitrate can be kept in a condition suitable for easy mechanical handling.

For use in conjunction with fuel oil an absorbent form of ammonium nitrate is required. This is produced by spraying a hot 95% solution down a high tower, so that some drying occurs before the spherical droplets reach the bottom. The resultant spheres must be carefully dried and cooled to prevent breakdown in handling. They are then usually coated with a mixture of diatomaceous earth and a wetting agent in approximate proportions of 0·5% and 0·05% respectively. The bulk density of the product is about 0·7 to 0·8 compared with about 1 for the dense material and it will absorb 7–8% of light oil without appearing unduly wet. Ammonium nitrate "prills" of this type were originally made in Canada, but have since become popular in many parts of the world.

Ammonium nitrate undergoes phase changes at 32° and 83°C and melts at 170°. It is not normally considered an explosive when pure, although under suitable conditions it can be made to detonate. When mixed with small amounts of organic matter it becomes much more sensitive and several serious explosions have occurred with such mixtures. The limit of organic matter so far allowed in the U.K. is 0·05%, but in some countries 0·1% is accepted.

Nitroglycerine

Nitroglycerine, or glycerine trinitrate, has the following formula:

$$H_2CONO_2$$
$$|$$
$$HCONO_2$$
$$|$$
$$H_2CONO_2$$
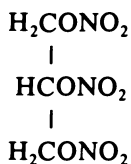
It was discovered by Sobrero in 1847, but was developed to a commercial scale by Nobel. It has for a long time been, and still is, the most important sensitiser for commercial explosives.

Nitroglycerine is made by reacting purified glycerine with a mixed acid

containing nitric acid, sulphuric acid and water. The temperature must be carefully controlled and the product when separated from the refuse acid has to be washed free from surplus acid before it becomes stable. It is a sensitive explosive, easily initiated by certain forms of friction and impact. For this reason and because of the importance of economic production of the compound, considerable study has gone into the design and operation of nitroglycerine plants.

Originally nitroglycerine was made by batch processes in which glycerine was added slowly to mixed acid in large vessels containing cooling coils. The acid contained 40–50% nitric acid with the remainder sulphuric acid. The worker controlled the flow of glycerine so that the maximum temperature allowed, usually 18°C, was not exceeded. Nitroglycerine, being less dense than the refuse acid, separated to the top and could be skimmed off. It was then washed with water and dilute sodium carbonate solution in air-stirred vessels before being allowed to stand and was then weighed for use. The nitration, weighing and washing were usually carried out in separate houses. Should any untoward incident occur during nitration, the whole mixture of acid and nitroglycerine could be discharged rapidly into a large volume of water in a drowning tank. As large quantities of nitroglycerine were involved, accidents when they happened were usually severe, and for this reason continuous processes involving smaller amounts of nitroglycerine in process at any time were evolved.

The first continuous process was that of Schmid in which glycerine and mixed acid were fed continuously into a specially designed, stirred and cooled nitrator; cooling was by chilled brine. The mixture from the nitrator went into a separator of special design from which the nitroglycerine overflowed from the top and refuse acid was removed from the bottom. The crude nitroglycerine was then washed in a series of columns and flowed by gravity to the weighing house.

A more recent process was developed by Biazzi and is somewhat similar in general principle to the Schmid process. It uses, however, improved chemical engineering designs and in this way is suited to operation by remote control.

The most recent process was introduced by Nitroglycerine AB (NAB) in Sweden and has a radically different system of nitration. An injector is used for mixing glycerine and nitrating acid and the nitration is carried out

in a tube. The mixture of acid and nitroglycerine passes through a tubular cooler and is then separated in a centrifugal separator. The short residence time makes possible the use of high nitration temperatures and the throughput of the plant is high. Nevertheless, only very limited amounts of nitroglycerine are in process at any time.

Nitroglycerine can detonate in pipes of diameter down to approximately 5 mm. In nitroglycerine manufacture there is, therefore, an inherent danger of transmission of detonation from one manufacturing house to another in the series. Even a pipe which has been emptied of nitroglycerine can have on it a skin of the product sufficient to enable transmission of detonation from one end of the pipe to the other. To prevent the spread of an accident it is now usual to transfer nitroglycerine as a non-explosive emulsion in an excess of water. Such emulsion transfer is particularly convenient with the NAB process, as the emulsion transfer lines can also carry out the necessary process of washing and purification.

Nitroglycerine is a viscous yellow liquid which freezes at $13 \cdot 2°C$ to a sensitive solid explosive. Because of the danger of freezing, pure nitroglycerine is now only rarely used in making explosives. The common practice is to mix ethylene glycol with the glycerine and nitrate the mixture so as to give a product which contains from 20 to 80% of ethylene glycol dinitrate. For most climates any mixtures in this range give satisfactory results, although under the very coldest conditions the extremes should be avoided.

Nitroglycerine when heated rapidly explodes somewhat above 200°C, but on storage it proves unstable at temperatures exceeding 70–80°C. The thermal decomposition products are very complex. In large quantities of water it is hydrolysed to nitric acid and glycerine, but this reaction is very slow at ordinary temperatures. Nitroglycerine has a marked physiological effect producing dilation of the arteries and severe headaches. Ethylene glycol dinitrate, or nitroglycol, has even more severe effects and with a higher vapour pressure is more prone to cause unpleasant reactions. It is also more toxic than nitroglycerine. These effects call for precautions during manufacture, but are not severe enough to affect the user.

Nitrocellulose

Nitrocellulose is used in commercial high explosives mainly to thicken

the nitroglycerine in the preparation of gelatine and semi-gelatine compositions. The raw material is cotton. Nitration is carried out with mixed acid containing nitric and sulphuric acids and a proportion of water adjusted so that the nitrogen content of the nitrocellulose produced is about 12·2%. The relationship between the nitrogen content of the product and the acid left after nitration is shown in the ternary diagram (Fig. 4.1). Nitrators
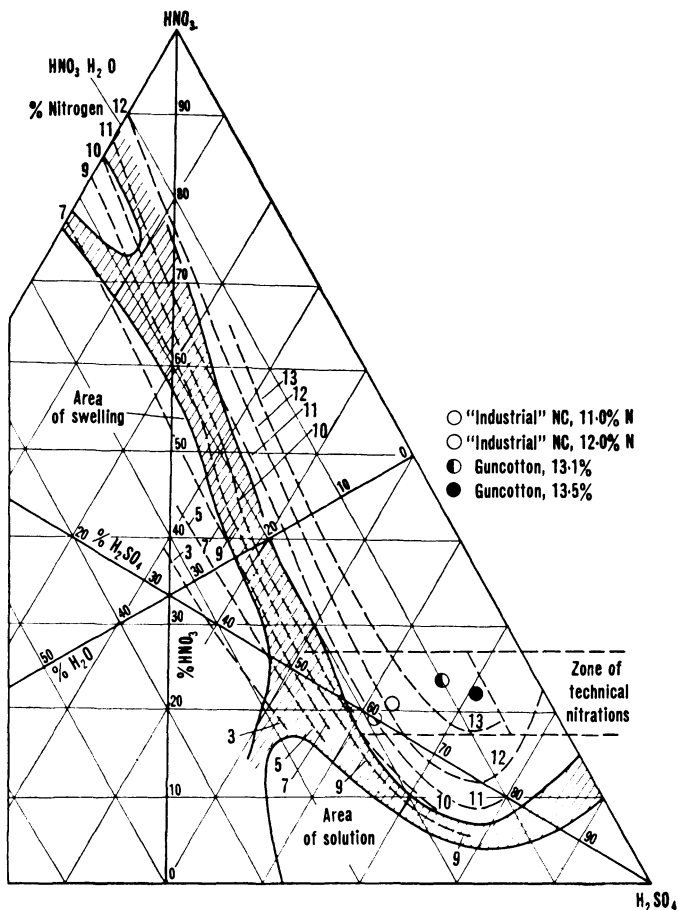

FIG. 4.1. Cellulose nitration diagram.

may be stirred or unstirred, depending on the nitration method used and the particular type of nitrocellulose required. After nitration, excess acid is removed in a centrifuge and the acid-wet nitrocellulose drowned in a stream of water. The nitrocellulose is stabilised by treating it with hot acidic water followed by hot dilute sodium carbonate solution. It is then pulped to a fine form so that it will dissolve rapidly in nitroglycerine.

The nature of the nitrocellulose used is of particular importance in explosives if freedom from exudation of free nitroglycerine during storage is to be avoided. Nitroglycerine is only a poor solvent for nitrocellulose and stability of the gel depends on continuous formation and breakdown of gelled structures. The distribution of nitrogen content and viscosity, even in the individual fibres of the nitrocellulose, is therefore of paramount importance.

Nitrocellulose is usually handled wet and containing approximately 30% of water. Under these conditions it can be considered as a non-explosive material when the nitrogen content does not exceed 12·6%. More highly nitrated cellulose is known as guncotton and is explosive even when moderately wet. When dry, nitrocellulose of all types is an extremely sensitive and dangerous explosive. Dry nitrocellulose is required for use in certain types of explosives and is then prepared by slow drying of the wet material in a current of warm air.

TNT

The preparation and properties of TNT are described in Chapter 3. Next to nitroglycerine, TNT is the most important sensitising constituent of commercial explosives. For such purposes it does not need to have the high purity demanded for the military product, but otherwise the material is identical.

In commercial explosives TNT has the advantage of greater safety in handling than nitroglycerine and also less physiological effect. On the other hand, it gives explosives which tend to be unreliable under certain conditions. Its use is therefore tending to diminish in Britain, although in some countries it is being applied in slurried explosives for large boreholes (see p. 56).

Powder Explosives

The preparation of powder explosives is in essence simple. In the case of mixtures of ammonium nitrate and fuel oil in particular, the only requirement is a method of mixing which does not cause undue breakdown of the absorbent grains of ammonium nitrate. Hand mixing is employed for small quantities, otherwise some form of rotating container or gently stirred vessel.

Powder explosives containing nitroglycerine are naturally more difficult to manufacture. Full precautions against explosion must be taken at all stages. The mixing equipment is generally a vessel containing a stirrer on a horizontal axis, or with two parallel stirrers as in the familiar Werner Pfleiderer type. In modern installations addition of ingredients and mixing and emptying operations are frequently carried out by remote control. The process consists simply of adding the ingredients to the equipment and stirring until adequately mixed, usually for a period of about 15 min. The mixed explosive is then cartridged, and for this purpose a variety of machines is available. In the commonest types, pre-formed waxed paper shells are placed under a row of nozzles and the powder explosive is then tamped or fed by worms into these shells. When the shells are sufficiently full, the spare paper at the upper end is closed over in a crimping operation. Cartridges can afterwards, if necessary, be further dipped in wax as an extra protection against ingress of moisture.

Powder explosives based on TNT are manufactured in a different manner. The commonest is to mill the TNT in large mills with suspended steel wheels which grind the explosive to a powder. Other ingredients are added and milling continued until the mixture is sufficiently fine and well mixed to have the required sensitiveness. Alternatively, the TNT and other ingredients can be mixed by stirring them together at a temperature above the melting point of TNT. Explosives so mixed are usually less sensitive but have improved resistance to moisture. Cartridging of TNT explosives is usually carried out with screws of the auger type with large open flutes. For blasting operations the filling is into pre-formed paper shells, which are afterwards dipped in wax. TNT explosives are also often used for larger charges employed in seismic prospecting and in this case are usually filled into tins to give complete protection against water even under hydrostatic pressure.

Semi-gelatine explosives (see p. 49) are manufactured and cartridged as powder explosives, although the presence of a thickened nitroglycerine base gives them properties which can approach those of gelatines.

Gelatine Explosives

Gelatine explosives contain a sufficient quantity of nitroglycerine thickened with nitrocellulose to give the mixture a plastic or gelatinous consistency. Advantage of this is taken in the manufacturing operations. To obtain the best results, it is desirable to ensure that at least a high proportion of the nitrocellulose is dissolved in the nitroglycerine before the other ingredients are added.

The original practice, still often employed, consists of weighing out the required amount of nitroglycerine on to nitrocellulose in a rubber-lined box; the two are stirred by hand and the mixture allowed to stand, sometimes for several hours. The resulting jelly is placed in a mixer which frequently takes the form of a bowl of figure eight section with two sets of revolving blades on vertical axes; the remaining ingredients are added and the whole mixed until uniform. Frequently hot water is circulated through a jacket round the mixer so as to speed the final gelation of the nitrocellulose.

More recently advances in the manufacture of nitrocellulose and in mixer design have enabled a much shorter process to be adopted. Bowl mixers with twin sets of blades on horizontal axes are employed most frequently, although various other designs have been found satisfactory. Practice is to add the nitroglycerine and nitrocotton and stir for a few minutes to enable gelation to occur. The remaining ingredients are then added and mixing continued for a further period. Mixers are usually arranged to tilt so that the mixed explosive is discharged into bogies or carrying boxes.

There are many ways of preparing cartridges of gelatinised explosives. The original method employed the screw extrusion of the plastic in machines very similar to those used for making sausages. The extruded cord was cut by hand and wrapped in paper. Many machines have been designed for carrying out such filling processes automatically, usually by extruding the explosive directly into pre-formed paper shells. One such

machine, developed by the DuPont Company, extrudes several cords downwards into shells simultaneously, and stops the extrusion when the required depth of filling has been achieved.

A recent cartridging machine is the Rollex, designed by the firm of Niepmann & Sons. This operates on an entirely different principle in that the explosive is first rolled into a sheet and then portions of this sheet are cut off and automatically wrapped in paper. It can also be used for cartridging semi-gelatine explosives.

Slurry Explosives

Plants for the manufacture of slurry explosives vary considerably from the simplest to fully automated. A simple plant for example can consist of a jacketed ribbon mixer; a hot nitrate solution is first made and the other solid ingredients and gelling agent are mixed in. Finally the cross-linking agent and any sensitisers are added. The mixture is immediately transferred to plastic bags or cartridges and it is in these that the actual cross-linking and cooling takes place.

The more sophisticated plants may be typified by the mix-trucks used for mixing slurries on site and pumping them direct into boreholes. Such a truck will have a number of hoppers and tanks containing pre-prepared hot nitrate solution; solid ingredients such as ammonium nitrate, aluminium powder and guar gum; and solutions of cross-linkers and gasifying agents. Controlled feeds from these are led to suitable points along a continuous mixing system and the product pumped direct to a borehole before cooling or cross-linking has occurred. The diameters of all hoses should be less than the critical diameter of detonation of the explosive so that the plant is intrinsically protected from detonation.

Packaging

The packing of explosives is a matter of importance if they are to reach the user in satisfactory condition. The original wooden boxes have largely been replaced by more efficient fibreboard cases, although certain authorities still insist on the former. In either case, provision of an adequate waterproof barrier is important to prevent moisture causing

hardening and desensitisation of the explosive. The cartridges are sometimes placed in cartons, containing 2·5 to 5 kg, wrapped in waxed paper and sealed with wax. More recently the tendency has been to obtain waterproofness by using a polythene layer inside the packing case and doing away with the cartons. The final case usually contains 25 kg of explosives.

Factory Construction and Operation

In the manufacture of high explosives, the possibility of accidental detonation must always be borne in mind and buildings are constructed and arranged so as to minimise the possible effects of such an explosion. The buildings are placed sufficiently far apart so that an explosion in one building will not cause sympathetic detonation in the other. Practical distances do not make it completely impossible for detonation in one house to leave all other houses unaffected, for two reasons:
1. Debris from the first building may be projected for long distances and can fall in other buildings, causing the explosive therein to explode.
2. Explosives must be transported through the factory between the buildings and can assist the propagation of detonation from one building to another.

To assist in safety, buildings are specially constructed according to one of two schemes:
(a) The buildings can be of light construction with the machinery placed as far as possible below the level of the explosive and therefore unlikely to be projected into the air. Such buildings are usually surrounded by a mound or barricade consisting of concrete or earth, and at least as high as the eaves of the building.
(b) The buildings can be completely enclosed by concrete and layers of earth. If the amounts of explosives involved are small, such construction can completely contain any accidental explosion. More generally, however, the purpose of the overmounding is to prevent shrapnel from an explosion in one building penetrating to the explosive in adjoining buildings.

The safety of operators for the processes of mixing and cartridging can

be much assisted by remote control. In this case a concrete block house is built outside the explosive building and the controls for the machine are placed in the block house. The process itself is viewed either by a system of periscopes, or by closed-circuit television. Such a method of working leads readily to semi-automatic or automatic processes.

Originally, equipment was made largely from wood or gun-metal and often rubber lined. These materials give the lowest hazards from friction with explosives. Nowadays, improved standards of engineering and of design have made it possible to employ stainless steel and plastics in the construction of explosive machinery with considerable increase in mechanical efficiency. In this way not only can processes be carried out more rapidly, but the quantity of explosive present at any time is reduced, with consequent increase in overall safety.

It is essential in explosive operations to avoid the presence of grit or extraneous materials. In Britain the general practice is to provide buildings with "clean" floors, which can only be approached by the donning of special shoes or overshoes. The carrying in of unnecessary objects and particularly ferrous tools is strictly forbidden, and, of course, the presence of matches or smoking materials is illegal.

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CHAPTER 5

Design of Commercial Explosives

THE design of explosives is a matter of major importance to the manufacturer. The explosives industries of the world are extremely competitive and it is essential that products should be as cheap as is possible. A range of products must be provided such that one of them at least will be suitable for every type of work for which explosives may be required. A typical range, apart from special sizes, would be about thirty.

Explosives contain oxidising and combustible ingredients, whether united in a single molecule or present in different chemicals. A proper balance is essential, particularly if the explosive is to be used in confined places, especially underground. The "oxygen balance" of an explosive is the percentage excess of oxygen in the composition. It is calculated, usually, on the unwrapped explosive, as, in practice, only a part of the wrapper (usually considered to be about a half) takes part in the chemical reaction. Too high an oxygen balance leads to the production of nitric oxide and nitrogen dioxide in the explosion fumes which, therefore, become toxic. Too low an oxygen balance, whilst having advantages in generally giving the explosive a higher power, leads to the production of excessive amounts of carbon monoxide which is also poisonous. The production of poisonous gases by explosives cannot be entirely eliminated, but by good design can be reduced to negligible proportions.

Complete reaction of explosives is important in obtaining the best results for both power development and fume avoidance. It is aided by the use of fine materials, but if this is carried too far other disadvantages of hardness and low density are introduced.

Some typical compositions of commercial explosives are given in Table 5.1.

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TABLE 5.1 *Compositions of Non-permitted Commercial Explosives*

Explosive	Explosive sensitiser		Oxidiser		Fuel			Miscellaneous	
	Nitroglycerine /nitroglycol	TNT	Ammonium nitrate	Sodium nitrate	Cellulosic	Aluminium	Oil	Nitrocellulose	Other
ANFO	—	—	94	—	—	—	6	—	—
NG powder	10	—	80	—	10	—	—	—	—
NG semi-gelatine	15	—	77·1	—	6	—	—	0·4	1·5
Ammon gelignite	32	—	60·5	—	6	—	—	1·0	0·5
NS gelignite	60	—	—	29	7	—	—	3·5	0·5
High velocity gelatine	50	—	—	29	9	—	—	2	10
Blasting gelatine	91·4	—	—	—	—	—	—	8	0·6
TNT powder (strong)	—	10	85	—	—	5	—	—	—
TNT powder (normal)	—	10	86	—	4	—	—	—	—

Ingredient %

ANFO

The simplest explosive to design is ANFO, or ammonium nitrate mixed with fuel oil. The choices to be made here are the grades of ammonium nitrate and oil and the proportion in which they are mixed.

As noted above (p. 36), the ammonium nitrate used for these explosives should be porous and should retain 7% of the oil without tendency to segregate on standing. A further requirement in modern practice is that the mixture, when blown into boreholes by compressed air, should break down to give a proportion of fine powder which increases both the density of loading and the sensitiveness of the mixture (see p. 141).

The oil used should be of a volatile type, as the more volatile oils gives the greatest sensitivity. However, the use of petroleum fractions with too low a flash point is hazardous. The choice is, therefore, usually made of a fuel oil similar to those used for diesel engines. It is common practice to add a proportion of dyestuff to the oil, partly to make adequate mixing of the explosive immediately visible, and partly to assist the user in seeing proper loading of boreholes, particularly in salt and other white materials.

A choice of composition is generally determined by the necessity for oxygen balance. A range of 5·5–6% of fuel oil gives a balanced mixture which produces negligible poisonous fume and maximum power on detonation. For certain uses, as in quarries, lower proportions of oil are sometimes used, as 2–3% of oil gives maximum sensitiveness to initiation; such compositions are, however, unsuitable for underground use as they produce nitrogen dioxide on detonation.

Nitroglycerine Powder Explosives

Another type of explosive which is of relatively simple design is the nitroglycerine powder explosive. This type of explosive is made from ammonium nitrate, sometimes with sodium nitrate, a combustible material, and nitroglycerine as a sensitiser. As this is essentially a cheap type of explosive, the relatively expensive nitroglycerine component must be kept to the minimum possible value. Figures as low as 6% have been used, but general practice for smaller sizes of cartridges is 8 or 10% so as to ensure adequate sensitiveness and reliability of propagation. If more

than 10% of nitroglycerine is included, care is needed to ensure that the liquid does not tend to leak out of the explosive on standing.

As nitroglycerine itself is nearly oxygen balanced, the mixture of ammonium nitrate and fuel used in a powder explosive should also be approximately oxygen balanced. The actual proportions depend on the nature of the combustible chosen and this choice is in itself dependent on the explosive properties required. In general, the aim is to obtain the highest strength per unit volume and this is achieved by attaining the maximum density possible in the explosive. To this end, the ammonium nitrate must be used in a dense form. The choice of combustible is more restricted because it must not be bulky but must still be absorbent enough to retain the nitroglycerine in the explosive. For economic reasons, one of the commonest choices of combustible is a fine form of sawdust, known as woodmeal, made from selected woods, as this gives a suitable combination of density and absorption.

There is always a search for higher power in explosives, and one common way of achieving this end is to add materials which liberate the maximum energy on combustion. Of such materials, the only one which has achieved common usage is aluminium, but such others as silicon and ferro-silicon have been considered. Magnesium is in general too reactive chemically to be safe on storage. Aluminium, when added, is used in a relatively fine, sometimes flake, form as in this condition it increases the sensitiveness of the explosive as well as the power. Aluminium, indeed, is frequently added to ANFO for similar reasons, but the greater sensitiveness of the resulting explosive makes it suited only to manufacture in specially designed premises, and in most countries it is not considered safe for such an explosive to be made with simple equipment on the site where it is used.

Semi-Gelatine Explosives

The strength of nitroglycerine powder explosives is limited to about 80% blasting gelatine and the density to approximately 1. To achieve greater concentrations of energy it is necessary to increase the nitroglycerine to an extent such that it can no longer be absorbed by the other ingredients of the powder explosives. When this stage is reached,

nitrocellulose must be added to the nitroglycerine to prevent exudation from the explosive cartridges. This leads to the semi-gelatine type of explosive which forms a rather indistinct class between the powders and the gelatines. The true powder explosives contain no nitrocellulose and, therefore, can only be made at relatively low densities and are also susceptible to the action of water. The true gelatine explosives, on the other hand, have a continuous phase of gelled nitroglycerine and, therefore, have a high density and are relatively unaffected by water for an appreciable length of time. Semi-gelatine explosives can be made with proportions of nitroglycerine from 10 to 30% and with properties which range over the extreme limits between powders and gelatines.

The choice of composition of a semi-gelatine depends ultimately on two requirements, namely the strength required and the resistance to water needed for the particular application. For economic reasons the lowest nitroglycerine content which satisfies both these requirements is always chosen.

With mixtures of ammonium nitrate and ordinary combustibles, the highest weight strength (see p. 61) which can readily be achieved is about 85% of blasting gelatine. To obtain high bulk strength it is, therefore, necessary to increase the density to the maximum possible. In practice, the maximum density usefully achieved is about 1·25 and this with relatively dense combustibles means a nitroglycerine content of 15–20%. If either the ammonium nitrate or the combustible available is not of high density, increased quantities of nitroglycerine may be necessary. As with powder explosives, alluminium may be added to give extra power, although this is not necessarily economic.

An explosive designed as just stated would give very satisfactory results for many purposes when used in dry or almost dry conditions. Underground, however, boreholes are frequently very wet and in work above ground running water is often encountered. Semi-gelatine explosives, aluminium may be added to give extra power, although this is not necessarily economic.

consist in general of sodium carboxymethylcellulose, starches, or natural gums, prepared in a way to swell rapidly in contact with water. A small percentage of such an additive has little effect on explosive properties, but should the explosive come into contact with water, the gum on the outside layers immediately swells to form a gelatinous layer which impedes further

ingress of the water. Such protection cannot be permanent, but with suitable design it can last for a number of hours sufficient to enable boreholes to be loaded and fired.

Gelatine Explosives

Gelatine explosives are more costly in raw materials than the powder or semi-gelatine types, although this can to some extent be offset by greater ease, and therefore less expense, in manufacture. Their popularity throughout the world rests on a number of important advantages over other available explosives:

1. They provide high bulk strength.
2. They are very resistant to the effects of water.
3. Under conditions of use they propagate extremely well from one cartridge to another, so that failures are unlikely even under bad conditions.

In designing a gelatine explosive, the same questions must first be answered as in the case of all other explosives, namely, the bulk strength required and the degree of resistance to water. Again the practical requirement is to provide these properties with the minimum proportion of nitroglycerine.

Blasting gelatine, containing 92% of nitroglycerine and 8% of nitrocellulose (usually also small amounts of chalk) is the strongest and most water-resistant of these explosives. Cartridges have in fact been fired successfully after being left accidentally for many years immersed in water. Although for economic reasons blasting gelatine is little used nowadays, its properties are of importance in understanding those of other gelatine explosives and the principles of their design.

If the most uniform obtainable nitrocellulose of nitrogen content about 12·2% is dissolved in nitroglycerine (containing nitroglycol) and the solution made as complete as possible, by heating and prolonged standing (and particularly with the assistance of gelatinising accelerators such as dimethylformamide, or certain ketones and esters), a clear yellow gel can be obtained. Vacuum mixing is necessary to avoid the occlusion of air. Such a gel has two unexpected properties. In the first place it is extremely difficult to initiate this explosive, a primer as well as a detonator being

required. Secondly, the explosive on standing tends to exude liquid nitroglycerine. These tendencies are present in all gelatine explosives and must be avoided by careful design.

Control of exudation depends mainly on the suitable choice of the nitrocellulose used. Some lack of uniformity in this product is certainly desirable. This offers no serious difficulty, although it is necessary to ensure a constant watch on manufacturing processes to see that quality is maintained. In other gelatine explosives, particularly those containing ammonium nitrate, exudation can be induced by slow chemical reaction. The addition of alkalis, for example, can liberate ammonia which in turn can react with nitrocellulose and cause it to lose its power of binding nitroglycerine. Such effects are accelerated at high temperatures and under wet conditions and it is usual practice to test all explosives under such adverse conditions before they are put on the market.

Blasting gelatine as normally manufactured is easily initiated by commercial detonators. This has been shown to be due to the trapping of small bubbles of air in the explosive during the operations of mixing and cartridging. Such an explosive shows two velocities of detonation, one at about 2000 m s^{-1} with low strength initiators, called the low velocity of detonation, and the other approaching 7000 m s^{-1} with high strength initiation, called the high velocity of detonation. This high velocity of detonation tends to fall as the degree of aeration is increased, but at the same time the minimum detonator strength needed to produce it is also decreased. These air bubbles are effective only within certain limits of size; thus during storage the explosive loses sensitiveness because the bubbles gradually coalesce into larger and ineffective bubbles, and indeed the density of the explosive increases due to loss of air. The rate of these changes depends on the type of nitrocellulose used and special grades are necessary if explosives of this type are to remain easily initiated after long storage under adverse conditions.

In other explosives of a gelatine type some form of combustible is normally present. Most combustibles contain pores which hold air and they also assist mechanically in the trapping of air bubbles in the explosive. As a result, the lower the nitroglycerine content of a gelatine explosive, the easier it is to obtain adequate sensitiveness to commercial detonators. In the particularly difficult cases such as the higher strength gelignite

explosives, it is advantageous to add a proportion of a low density combustible, such as dried sugar cane pith.

Gelatine explosives, initiated by commercial detonators, will normally fire at the low velocity of detonation initially, although this may well build up quite quickly into the high velocity. For some applications a high velocity of detonation is essential. This can be ensured by the addition of barium sulphate, or other material with density exceeding 2·8, in a fine form. Such additives have the property of ensuring rapid transition to the high velocity of detonation. This is, for example, of particular importance when the explosive is to be fired under a hydrostatic head, as in submarine work.

The other important factor in the design of gelatine explosives is the consistency of the product, which must be suited to the manufacturing facilities available, and which must remain usable throughout the life of the explosive. This entails that there should be a suitable balance between the solid and gelatinous phases of the explosive, the former not being too bulky and the latter not being too thin or too highly gelled. The explosives of this class, which are the most popular because they are the cheapest, usually contain the minimum proportions of nitroglycerine. Commonly, they can include also nitrobodies such as dinitrotoluene which are soluble in nitroglycerine and therefore assist in increasing the proportion of the liquid phase. When allowance is made for absorption by ammonium nitrate and by solid combustibles, nitrocellulose is added to an extent necessary to bind the nitroglycerine into the explosive. If the proportion falls, however, much below 1% on the total composition, the nitroglycerine phase becomes too fluid and the explosive tends to have reduced cohesion. At the same time, the large relative volumes of the solid phase make the explosive more sensitive to hardening under adverse conditions of temperature and humidity. These are the factors which effectively limit the extent to which the nitroglycerine content of such explosives can be reduced in efforts to attain economy.

The most important explosives of this class are the ammon gelignites, so called because they are based essentially on ammonium nitrate which is the cheapest and most powerful source of oxygen. Sodium nitrate is sometimes added as well in order to improve the oxygen balance for certain types of these explosives. The ammon gelignites are explosives with

density about 1·45 which can be made in all powers up to nearly 100% of blasting gelatine strength. They have good resistance to water and can be used freely under most wet conditions. In time, however, the ammonium nitrate, being extremely water soluble, is leached out of the explosive, which then becomes insensitive.

For the wettest conditions where the high strength of blasting gelatine is not required, the explosives used are the straight gelignites based on sodium nitrate instead of ammonium nitrate. Because of the low explosive strength obtainable when sodium nitrate is used, the proportion of nitroglycerine in these explosives must be high. On the other hand, when properly made to ensure adequate sensitiveness, these explosives have exceptionally good storage properties and can be used under even the most adverse conditions of wet working.

It will be clear from the above that the optimum types of oxidising materials are those of highest density and dense forms of ammonium nitrate are always used. The combustibles can be dense also, although it is sometimes necessary to add at least a proportion of the combustible in an absorbent form to ensure adequate sensitiveness. Wheat flour may be regarded as typical of a dense combustible; woodmeal is a useful and cheap combustible of intermediate properties.

TNT Explosives

The oxygen balanced mixture of ammonium nitrate and TNT contains 79% of ammonium nitrate and 21% of TNT. It has a power of about 85% of blasting gelatine. As a commercial explosive it would normally be considered too expensive because of the high proportion of the expensive TNT ingredient. Practical explosives of this type contain less TNT, usually in the range of 10–15% for explosives to be used in small diameters (below 5 cm) and 5–10% for explosives to be used in larger sizes. Oxygen balance is then achieved by the addition of any cheap finely divided combustible.

If the explosive is to be mixed hot, a fairly fine grade of ammonium nitrate is advantageous, as its high surface area gives a high reaction rate and therefore maximum sensitiveness in the explosive. Compositions intended for mixing in edge-runner mills are ground together in the process so that the type of ammonium nitrate or TNT used becomes of much less

importance. Indeed, a friable form of ammonium nitrate is often useful in reducing the time of mixing.

Simple mixtures of this type have little resistance to water and are suitable for use only under the driest conditions. Many methods have been used for giving water resistance to these explosives, particularly to the milled varieties which tend to be less satisfactory in this respect than the hot mixed compositions. A small proportion of wax may be used, particularly if mixed in hot, but this tends to desensitise the explosive. Greater success is achieved by the addition of calcium soaps such as calcium stearate, in finely divided form. These also cause some desensitisation, but to an extent which is less marked in proportion to the degree of waterproofness achieved.

A proportion of finely divided aluminium is often added to TNT explosives in order to increase the power. As aluminium has also a sensitising effect, it is particularly useful in waterproofed compositions. Another power producing additive which is sometimes employed in large diameter charges where its slow reaction is of less disadvantage is calcium silicide. Care must be taken with this material, however, to ensure that it does not lead to sensitiveness to friction and impact.

Slurry Explosives

Slurry explosives, also known as water-gel explosives or dense blasting agents, resulted from the work of M. A. Cook and others in North America and have now found world-wide application particularly for large scale operations. Whilst slurries are made in many forms to suit almost all types of use, they may be divided into two essentially distinct types:

1. Dense slurries which are not aerated and therefore have a density of about 1·4. The required sensitivity is achieved by the addition of substances such as TNT.
2. Aerated slurries, where sensitivity is attained by introducing air or other gaseous bubbles to give densities ranging from 1·05 to 1·3 according to the proposed use. The practical lower limit to the density is usually set by the requirement that the explosive should not float to the surface in a water-filled borehole.

In either case the base of the explosive is an aqueous solution of

ammonium nitrate with another nitrate such as that of sodium or calcium. Compared with ammonium nitrate alone, such mixed nitrate solutions contain less water and therefore give increased explosive power; in addition they are more easily sensitised and retain their properties better at low working temperatures. The nitrate solution is thickened by addition of guar gum which is then cross-linked, typically by adding a chromate. The base of the explosive is therefore a more or less rigid gel, the term slurry being in fact rather inappropriate.

The process of gelling is of importance as it imparts water-resistance which makes it possible to use the final explosive under wet conditions. Particularly for explosives which have to be stored before use, careful control of gelling is necessary to ensure retention of sensitivity and absence of physical breakdown. Suitable grades of gum and cross-linker must be used and an appropriate pH of the solution maintained.

This base is used to the minimum possible extent in the final explosive as the water it contains does not contribute to the power and indeed requires energy for its evaporation. All slurry explosives therefore contain further ammonium nitrate in solid form and also a fuel for combustion. The ammonium nitrate is usually in dense form similar to that used in nitroglycerine explosives as this gives the best physical properties. However, it is common practice to mix the explosive hot so that much or all of the solid ammonium nitrate results from crystallisation during cooling.

The gums and other ingredients can often provide much of the necessary fuel but the addition of aluminium has special advantages. Aluminium gives a highly energetic reaction in these explosives and helps to remedy their otherwise low power. The metal must be finely divided if it is to react completely in the borehole. It must also be relatively pure, otherwise even in the presence of chromates it will react with the aqueous base at room temperature to give gassing and instability. Other energetic fuels which have been used with some success are silicon and ferro-silicon, but these tend to be slow in reacting during detonation.

The first and still successful dense slurry was sensitised with TNT and therefore consisted of a suspension of TNT and solid ammonium nitrate in a solution of ammonium and sodium nitrates gelled with cross-linked guar gum. The TNT is preferably in the form of small pellets. No further fuel than the TNT is essential but aluminium can be added for increased

strength. The degree of sensitivity which can be achieved with TNT is limited and it is usual to fill the slurry in plastic cylinders 10 cm or more in diameter. If required the plastic can be slit immediately before use to allow the explosive to slump and completely fill the borehole. Initiation is by booster, such as cast pentolite.

More recently isopropyl nitrate has been used in place of TNT for sensitising dense slurries. Although not itself explosive, this liquid gives a sensitivity at least equal to that obtained with TNT, whilst at the same time reducing the proportion of aqueous base and therefore water needed in the composition. Dense slurries have also been made with such ingredients as pentolite and smokeless powder as sensitisers but these have no special advantages and are usually uneconomic.

The more widespread current use of slurry explosives is undoubtedly due to the development of aerated slurries. These have much greater versatility than the dense variety and can be made to a wide range of sensitivity, density and power. Moreover they are particularly suited to manufacture on site for pumping direct into a borehole without intermediate packing and transport.

The sensitivity depends on the presence of gas bubbles, but to be effective these bubbles must be of suitable size. The following are the most important ways of achieving the required result:

1.   Mechanical entrapment of air.
2.   Introduction of microballoons—i.e. hollow spheres of plastic.
3.   Production of gas in the explosive by chemical reaction.

Mechanical aeration by prolonged mixing alone is not an effective means of sensitisation as the bubbles produced are predominately too large. The addition of some material which facilitates the occlusion of small air bubbles is therefore necessary. A particularly useful material of this type is paint fine aluminium. This material, used in the manufacture of paints and lacquers, consists of beaten flakes of aluminium made water-repellent with a coating such as a stearate. When stirred into a slurry explosive the flakes are only imperfectly wetted and retain adhering to them small bubbles of air which are very effective in sensitising the slurry. For best results it is necessary to carry out the addition of the aluminium carefully and as the final stage of the process of manufacture; moreover the base of the slurry must be of optimum consistency. Used in this way only a few per cent of paint fine aluminium can give a slurry explosive

which is sensitive to a commercial detonator. Although the gap sensitiveness is likely to be low compared with explosives based on nitroglycerine, these slurries can be used with care in small diameters and by variations in other ingredients can be designed for all general purposes including permitted explosives of the P1 and P3 types. Disadvantages of this type of slurry however are that paint fine aluminium presents special handling difficulties in explosives manufacture and that it is expensive even in the small quantities required.

Air can also be introduced with the help of the thickeners, either guar gum itself or alternatives such as other natural gums or starches. Part of the total gum is first dissolved in the aqueous base, without cross-linking. Addition of the remaining gum to this pre-thickened solution automatically occludes air bubbles which can be stabilised by cross-linking. This process is particularly suited to slurries mixed on site; in this case the process of cross-linking is critical and often controlled by activating the chromate by adding a small proportion of a reducing agent.

Microballoons have the advantage of giving a well controlled addition of sensitiser and also improved stability on storage. They are however less effective than direct gas occlusions when measured at constant explosive density and therefore tend to have most use in conjunction with the soluble additives described below.

Chemical production of gas, for example by the decomposition of dissolved hydrogen peroxide, is again a very controlled method of sensitisation. The same method can be used for adjustment of the final density of the explosive. Thus a small addition of a peroxide gives an explosive of adequate sensitivity for large boreholes together with maximum density and bulk strength of explosive. To attain the sensitivity needed for smaller boreholes it is only necessary to increase the addition of peroxide, although there will of course be a reduction in density and bulk strength.

It has been pointed out that the water present in a slurry explosive must be vaporised during detonation and thus absorbs energy. Although the water vapour increases the total volume of gas produced the nett effect is still a reduction in strength. Many attempts have therefore been made to find a soluble additive which will replace part of the water to give both increased power and sensitivity. One such substance which has found success is ethylene glycol mononitrate. This when pure is explosive, but for

use in slurries it can be handled throughout in safe solution form. Another such substance is mono-methylamine nitrate which again is handled in solution. In both cases there is an increase in power and sensitivity but in most practical applications further power is attained by the addition of aluminium and the sensitivity is increased by the addition of microballoons or by gassing.

In many ways slurries may be considered as intermediate between ANFO and nitroglycerine explosives. They are more expensive than ANFO but can be used in wet conditions; they are often cheaper and safer than nitroglycerine explosives but are more critical of conditions of use if misfires are to be avoided.

Other Explosives

For reasons of safety it is always desirable to use the least sensitive explosive which is adequate for any given operation. This has led to development of a class of explosives which in the United States are called nitrocarbonitrates. These explosives contain no self-explosive ingredient and are themselves insensitive to initiation by a single commercial detonator of ordinary strength. More important, when they are properly designed they are insensitive to impact and friction and unlikely to detonate when involved in a fire. Such explosives are usually based on ammonium nitrate, sensitised with nitrobodies, typically dinitroluene. Ordinary combustibles may well be added to give oxygen balance, and waterproofing ingredients similar to those used in TNT explosives may also be considered desirable. The addition of most power producing ingredients such as aluminium, however, is unwise in view of the reduction in safety to which they lead. Explosives of this type must be used with adequate care, either in large diameter holes, or else sealed in tins for oil prospecting. Although relatively safe, they are still explosives and should be handled as such.

A type of explosive, not based on nitroglycerine or on TNT, which achieved popularity for a time and is still used in some countries, is the liquid oxygen explosive or LOX. This is made on the site of the blasting operations by immersing in liquid oxygen a pre-formed cartridge of absorbent charcoal. Charcoal saturated with a suitable proportion of

liquid oxygen is readily detonated by a commercial detonator. The cartridge thus prepared is loaded and fired before the oxygen evaporates. For large-scale operations this represents a very cheap way of preparing explosive. Unfortunately, the process is dangerous for reasons not fully understood and the history of LOX explosives is marred by a series of fatal accidents. For this reason, these explosives are little used today in most countries.

Before nitrates and particularly ammonium nitrate were readily available commercially, explosives were developed based on chlorates and perchlorates. These also are still used in some countries. In general perchlorates are considered less dangerous than chlorates and therefore preferred. They are easily sensitised, so that in addition to explosives of this type based on nitroglycerine, others have been based on various organic liquids, particularly nitrobodies. History shows that chlorates and perchlorates must be regarded as temperamental substances, liable in bulk to lead to inexplicable accidents. Particularly when mixtures of chlorates and oxidising materials are allowed to become wet and then dry out, conditions can arise in which there is an appreciable sensitiveness to friction and impact. Explosives of this type have an unfortunate record of accidents. They are used, therefore, to a limited extent only, now that safer compositions are available.

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CHAPTER 6

Assessment of Explosives

MUCH information concerning any given explosive can be obtained by calculating its properties on theoretical grounds. This is particularly valuable as the calculations indicate the performance which the explosive may have under ideal conditions, namely, infinite charges. In practice, such perfection is never achieved and it is a matter of practical importance to assess the properties of an explosive under conditions more appropriate to its use. Such an assessment is usually made by a series of tests chosen to measure the performances of the explosive under various conditions. Whilst these tests are of considerable value, particularly for comparative purposes, it must be remembered that no laboratory test or series of tests can predict precisely the performances of explosives which may themselves be used for widely varying purposes. It is obvious that the assessment of an explosive for use under water should follow different lines from the assessment of an explosive for use in a mine. It is less clear, but equally important, that the assessment of mining explosives should depend on the nature of the rock in which the mining is to be carried out. The ultimate test for all explosives is use in the field.

Power

The power, or strength of an explosive, is one of the most important properties of interest to the user. It is usually expressed in terms of power per unit weight, which is appropriate for comparing explosives used in charges measured by weight. It can alternatively be expressed as power per unit volume, which is appropriate for explosives which are used to fill boreholes of a given size. The relation between the two depends solely on the density, so that the one is readily calculated from the other.

The ultimate test used by NEC for commercial explosives consists in carrying out small-scale blasting operations in a quarry. The maximum weight of rock adequately broken per 0·5 kg of the explosive is calculated and used to indicate the power of the explosive. The rock involved is of fairly average nature for the district and the results therefore form a useful general comparison of strengths. Such testing is tedious and expensive and carried out only as a final assessment.

The maximum potential power of an explosive can be calculated, or it can be measured by techniques such as those developed by Cook. A typical method consists of firing the explosive under water and measuring the energy liberated in the various forms, such as shock wave in the water, the work of expansion of the gas bubble, etc. These figures have limited practical value as the methods of application of explosives are of low and variable efficiency. A more practical measurement of strength can be obtained by the measurement of cratering efficiency. This, again, demands considerable expense and also requires the availability of uniform rock.

Most measurements of strength are done by laboratory methods and of these the most satisfactory is the ballistic mortar. Various forms of mortar have been designed, but the method accepted as an international standard by the International Committee on the Standardisation of Test on Explosives at Sterrebeck, Belgium, in 1962 rests on a design by the DuPont Company of the U.S.A. and is illustrated in Fig. 6.1. This consists of a pendulum 3 m long, at the bottom of which is a bob weighing 333 kg. A shot is used of 12·37 cm diameter, weighing 16·6 kg, and fitting with a clearance of approximately 0·08 mm. Ten grammes of the explosive under test are wrapped in tin foil and fired with a standard copper detonator. The explosive ejects the shot on to rubber matting or into a mound of suitably non-abrasive mixture. The corresponding recoil of the bob is shown on a scale and is a measure of the energy imparted by the explosive to the system. The mechanical efficiency of the ballistic mortar has been shown to be rather low, but it is constant and results are reproducible. Gradual wear causes the efficiency to change during use, so that it is general practice to use standard explosive as a reference material. In Great Britain the standard explosive is blasting gelatine and results are expressed as a percentage of the strength of blasting gelatine. In the U.S.A. the standard is usually TNT and the results are expressed relative to that explosive.

In the ballistic mortar test the explosive is well confined and develops

almost maximum power. To give results more comparable with practice for explosives which are slow in reacting, tests have been devised in which the explosive is fired in a less confined condition. Such tests are, of course, arbitrary and the results must be compared directly with practical results.
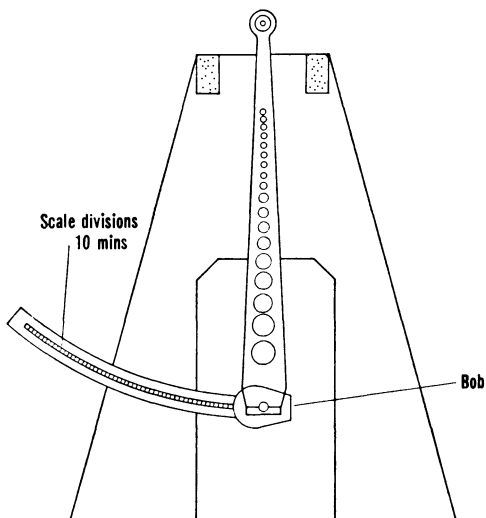

Scale divisions
10 mins

Bob

FIG. 6.1. Ballistic mortar.

An older form of measuring power was the Trautzl lead block test. This is illustrated in Fig. 6.2. The explosive under test is placed in a cylindrical hole in a block of specially cast lead and the remainder of the hole filled with sand. When the explosive is fired it causes an expansion of the hole in the lead block and this expansion is measured by filling with water. After subtracting the expansion caused by the detonator the result gives an indication of the strength of the explosive. This test has been particularly developed in Germany and the method adopted there has been accepted as an international standard. For most explosives there is an adequate correlation between lead block results and ballistic mortar measurement, as shown in Fig. 6.3. The lead block is less accurate for practical explosives, but is of value in studying weak explosives which are marginal in properties and therefore unsuitable for measurement in the ballistic mortar.
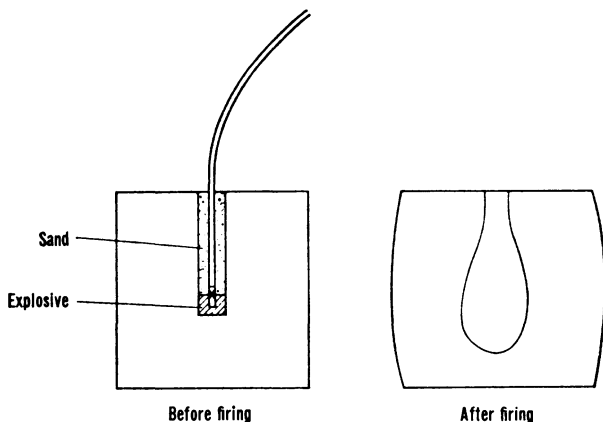
FIG. 6.2. Lead block test.

The ballistic mortar and lead block tests use only small amounts of
explosive and are not applicable to slurry explosives which are too
insensitive to detonate properly under such conditions. For these
explosives it is useful to fire larger amounts of several kg under water and
measure the period of oscillation of the gas bubble produced. The longer
the period the greater the energy of the gas bubble and this part of the total
energy of the explosive has been found to correlate well with the blasting
effect of the explosive.

Velocity of Detonation

A particularly valuable method of measuring velocity of detonation is
by high-speed camera, usually of a rotating mirror type. The layout is
illustrated in Fig. 6.4. A slit is placed in front of the explosive, or of an
image of the explosive in the optical system. This slit is in turn
photographed with the rotating mirror camera, the velocity of which is
known from stroboscopic measurements. As the detonation front is
luminous, the illuminated point travels along the slit and gives a
photograph consisting of a line inclined to the axis of the camera at an
angle which depends on the velocity of detonation and on the speed of
rotation of the mirror. By this method small charges can be studied and

constancy of velocity can be observed or any changes in velocity calculated.
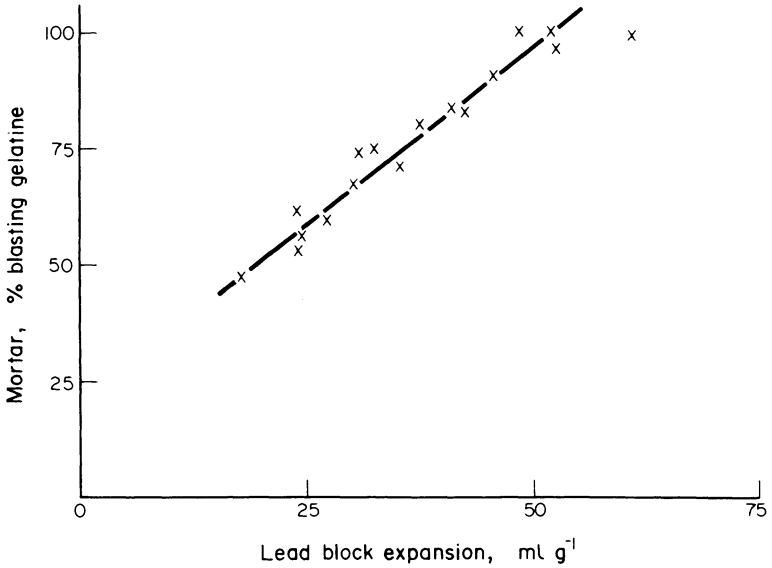
FIG. 6.3. Relationship between ballistic mortar and lead block tests.

Velocities can also be measured by electronic means and methods have been devised to give either continuous or intermittent readings. To obtain a
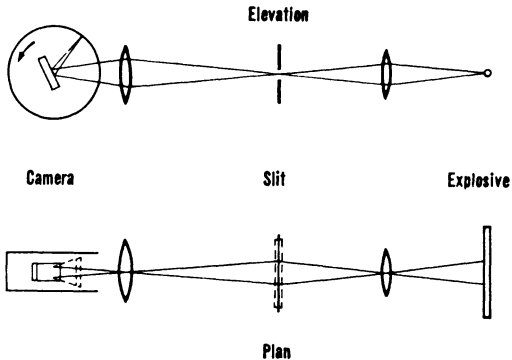
FIG. 6.4. Rotating mirror camera.

continuous record, a probe is placed along the cartridge, usually along the centre. This probe consists of a conducting rod around which is wound a helix of insulated wire. As the detonation wave passes along this wire, it breaks the insulation and brings the wire into contact with the central conductor. The resistance, therefore, diminishes as the detonation wave progresses along the cartridge. By recording the resistance on an oscilloscope with a suitable time base, the rate of progress of the detonation wave can be recorded.

As most explosives detonate at a constant speed, it is adequate in nearly all cases to record the average velocity along a given length of the explosive cartridge. To do this electronically two probes are inserted in the cartridge at a known distance apart, the first being sufficiently far from the detonator for the explosion wave to have become stabilised. The probes, may, for example, consist simply of two pieces of insulated wire wound together. The detonation wave in passing causes contact both mechanically and by its own ionisation. The two impulses received by a passage of current through the probes are caused to operate an electronic timer, which may in fact be calibrated directly to read the velocity of detonation of the explosive.

For routine use by unskilled personnel, the best method of measuring velocities of detonation is one due to Dautriche. The principle is illustrated in Fig. 6.5. The two ends of a length of detonating fuse are inserted in the explosive under test at a known distance apart. The mid point of the piece
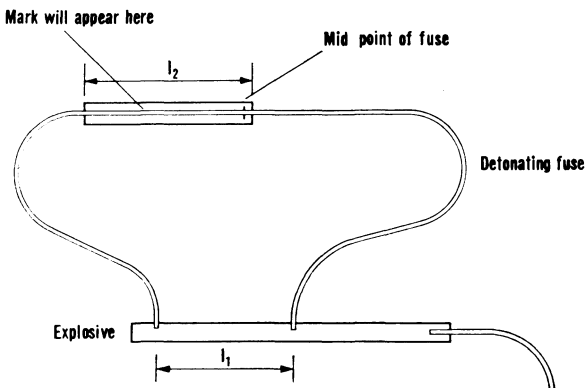
FIG. 6.5. Dautriche test.

of detonating fuse is known and the part of the fuse near this point is placed over a V-shaped groove in a thin lead plate. When the explosive is fired the fuse commences to detonate first at the end nearer the detonator and later at the other end. When the two detonation waves in the fuse meet they reinforce and produce a distinct mark on the lead plate, visible particularly as a split on the back. This point will be removed from the mid-point of the fuse by a distance which depends on the velocity of detonation of the explosive under test according to the following equation:

$$D = dl_1/2l_2$$

where D is the velocity of detonation of the explosive under test,

d is the velocity of detonation of the detonating fuse,

l_1 is the length of explosive under test,

l_2 is the distance between the centre of the fuse and the mark on the plate.

Thus by measuring the distance of the mark on the lead plate from the mid point of the fuse the velocity of detonation of the explosive under test may be calculated. In practice, it is simple to construct a rule by which the velocity can be measured directly from the lead plate.

Sensitiveness

The detonator sensitiveness of an explosive is measured by firing in it detonators of increasing strength. It is convenient to stand the cartridge of explosive vertically on a lead plate with the detonator at the top. The indentation produced on the lead plate then gives a good measure of the detonation of the explosive. The weakest detonators for this test contain only mercury fulminate. Stronger detonators have base charges of PETN, increasing in amount as the strength of the detonator is increased (see p. 102).

An equally important and more severe requirement for commercial explosives is that they should propagate in a train of cartridges. It must be remembered that in practice, when several cartridges are placed in a borehole it cannot be ensured that they are in contact and free from rock or coal dust between them. It is, therefore, necessary for the explosive to be able to fire over a gap, whether this be air or other substance. The Ardeer

double cartridge test (ADC test) was the first routine test of this nature. In this test two cartridges, as used in practice, are rolled at a selected distance apart in manilla paper. The assembly is placed on a flattened steel bar and fired from one end. The gaps are measured at which the second cartridge is detonated and also fails to detonate. Differences of distance of $1 \cdot 25$ cm at lower gaps and $2 \cdot 5$ or $5 \cdot 0$ cm at higher gaps are used. In the international test for gap sensitiveness, the paper is omitted and the cartridges are attached to a wooden strap which is suspended above the ground. For special purposes, such as with some modern weak coal mining explosives, a similar test can be carried out with the explosives enclosed in a cement or similar tube to simulate the confinement of a borehole. It is not normally necessary to do tests with materials other than air between the cartridges. In America, however, a test has been developed in which the sensitiveness is measured by placing increasing thicknesses of card or similar material between the cartridges.

(a)

(b)
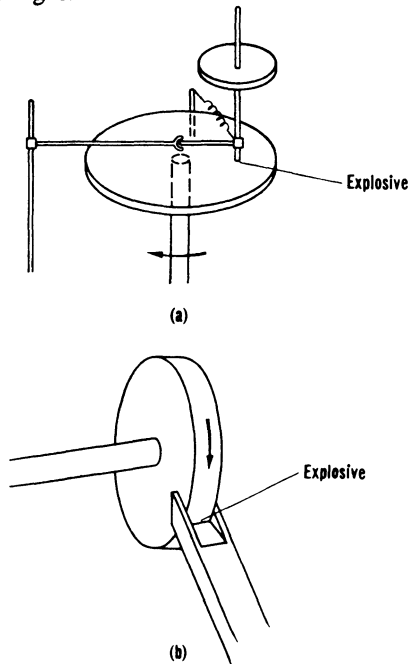
FIG. 6.6. Friction tests. (a) Liquid explosives. (b) Solid explosives.

Whilst an explosive must have adequate sensitiveness to initiation by detonators and to propagation of detonation through a train of cartridges, it must be sufficiently insensitive to friction and impact to be safe to handle. Sensitiveness to friction is commonly measured by some device as that illustrated in Fig. 6.6. The explosive is smeared on the surface of a rotating disc on which rests a rod of similar or dissimilar material, carrying a known weight. The speed of rotation can be varied and also the load employed. The higher the speed and the greater the load before initiation of the explosive occurs, the lower the sensitiveness of the explosive. Sometimes an oscillating plate is used instead of a rotating disc.

The sensitiveness of an explosive to impact is measured by determining the minimum height from which a given weight must be dropped in order to initiate detonation. Many forms of "fall hammer" test have been devised, the most important point of the various designs being the means adopted for retaining the explosive. A simple and practical method, used at Ardeer for many years, is shown in Fig. 6.7. In this the explosive is put
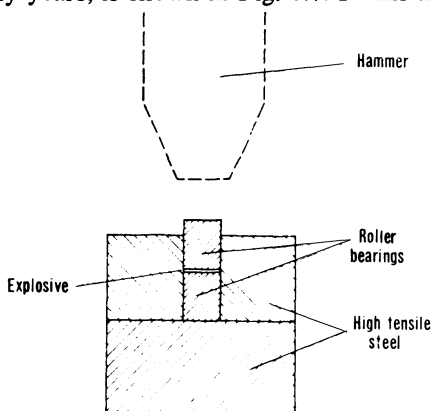
FIG. 6.7. Fall hammer test.

between two roller bearings, themselves placed in a ring of hardened steel and resting on a hardened steel base. The falling weight is arranged to hit the upper of the steel cylinders. The roller bearings must be changed after each ignition, as the condition of their surface markedly affects the results of the test. Similarly, the closeness of fit of the hardened steel ring is of importance. Typical weights employed are from 0·5 to 5 kg and heights of fall may be up to 200 cm.

A common hazard in the handling of explosives is for them to be subjected to the effects of a blow which is to some extent at a glancing angle. This corresponds neither to pure impact, nor to pure friction. A corresponding simple and useful test for the safety of an explosive during handling is the torpedo friction test illustrated in Fig. 6.8. In this, a torpedo
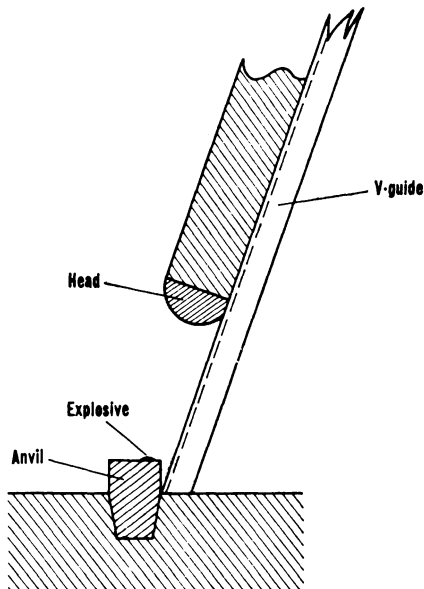

FIG. 6.8. Torpedo friction test.

weighing 0·5 to 5 kg slides down an inclined plane to strike the explosive resting on an anvil. The head of the torpedo and the material of the anvil can be varied according to the materials of construction of an explosives plant, or can be kept as mild steel in each case if an indication of relative hazards of explosives is to be obtained. The angle of fall is commonly 70 or 80°.

Numerous tests for safety have been described in the past. It is probably far less important what test is employed than that some test should be undertaken before any explosive is handled on any but the smallest scale. All tests of the safety of explosives are in fact relative, so that the particular test employed is a matter of convenience. As the presence of grit reduces

the safety of explosives, tests are usually repeated after a quantity of fine sand has been added.

Results of sensitiveness tests on typical explosives are given in Table 6.1, for steel to steel surfaces, in the absence of grit.

TABLE 6.1 *Sensitiveness of Explosives*

Explosive	Fall hammer (0·5 kg)(cm)	Torpedo friction (1 kg at 80°)(cm)	Friction wheel (0·5 m s⁻¹)(kg)
TNT	> 200	80–120	> 50
RDX/TNT	80–100	40–45	
RDX	25–30	10–20	
PETN	60–80	35–40	10
Gelignite	5–10	40–60	4
Ammon gelignite	30–40	40–60	30
NG powder	20–30	>150	> 50
TNT powder	160–200	100–120	> 50

Stability on Storage

All explosives are kept in magazines before use for periods which may be up to several years. These magazines are normally buildings which have neither special heating nor cooling, so that the temperature can vary widely in different parts of the world. Throughout this storage it is important that the explosive should remain safe and also retain satisfactory properties.

Explosives are exothermic in decomposition and can be considered as being in a metastable condition. To determine whether instability can set in, it is necessary to subject the explosive to conditions which are more severe than those occurring in practice. This in effect means that the explosives must be subjected to a higher temperature than those normally encountered. Unfortunately, as the temperature is increased the type of decomposition reaction changes, so that experiments at the highest temperatures, although rapidly carried out, do not necessarily indicate the stability of the explosive under practical conditions. The ultimate test of stability of an explosive must remain the maintenance of that explosive for several years at a temperature which somewhat exceeds the highest which is to be expected in practice. Common temperatures range from 35° to 50°C. To obtain a quicker indication of the stability of an explosive, tests

are carried out at higher temperatures. Storage at 60°C for several months gives useful information on the properties of an explosive, both chemical and physical.

In determining stability by the above tests, it is usual to note the onset of mass deterioration in the explosive. To obtain rapid results in the course of hours or minutes, it is necessary to modify the tests so as to determine the initial stages of decomposition. Many tests have been devised in which the explosive is heated at a relatively high temperature and the extent of initial decomposition determined by measuring the amount of gas evolved or the amount of acidity generated. Probably the best known of these tests is the Abel heat test in which a small amount of the explosive is heated (often at 70°C) and the time determined in which the gases liberated will produce a standard coloration on a starch–iodide paper. In Britain it is a legal requirement that explosives and their explosive ingredients shall satisfy this test for times in the region of 10 min depending on the class of explosive. The heat test, like all similar tests, does not measure the true stability of an explosive, although an unstable explosive cannot give a good result. It can be markedly affected by minor impurities which have no effect on the long-term life of the explosive, and the trend of the results with time is frequently more important than the results themselves. Rapid tests are invaluable as a control of production in comparing one batch of explosive with another; their application to new explosives can, however, be very misleading.

For nitrocellulose, including guncotton, the most suitable stability test is the B and J (Bergmann and Junk) test in which 2 g dried material is heated for 2 h at 132°C, the gases evolved being dissolved in water. The nitric acid in this water is reduced to nitric oxide, which is measured by volume.

For PETN and similar military explosives a valuable test is a vacuum stability test, in which some of the explosive is heated in vacuum and the rate of evolution of gas measured.

Apart from maintaining chemical stability on storage, an explosive must also maintain its physical form and its sensitiveness. Explosives containing nitroglycerine would, for example, be dangerous if they exuded nitroglycerine during storage. To determine these properties there is no real alternative to storing the explosive and examining it afterwards. The length of storage can, however, be reduced by marginally increasing the temperature during the period.

Fume

The fume from an explosive is best determined by firing a round in a part of a mine which can be completely cut off from the circulating air. After the air and fume have been circulated by a fan for a sufficient period, samples of the resulting mixture are taken and analysed.

Results of value can also be obtained by firing the explosive in a steel vessel reinforced with concrete. Care must be taken that by the use of lead tube or similar method the explosive is adequately confined, as unconfined explosives can produce abnormal fumes.

In measuring the nitrogen oxides produced by explosives, it must be remembered that ammonium nitrate can be left unreacted in small amounts from explosives containing this substance. The method of analysis adopted should, therefore, be insensitive to ammonium nitrate, for example the Griess–Ilosvay method. The composition of the gases will change with time, as the oxidation of nitric oxide to nitrogen dioxide at these low concentrations is extremely slow. A common procedure is to determine nitrogen dioxide after a period sufficient to allow oxidation to be complete. Carbon monoxide in the gases can be estimated by reaction with iodine pentoxide.

Whilst carbon monoxide and nitrogen oxides are the toxic products of explosives, other constituents of the fume cause a characteristic smell. As the nitroglycerine content of explosives is reduced, this smell tends to become rather unpleasant. Subjective tests must be used for its estimation.

Miscellaneous

Of other tests which are sometimes applied to high explosives, mention should be made of the tests for brisance. Brisance is an ill-defined word, best described by saying that an explosive of high brisance, when fired unconfined on a steel plate, will bend or shatter that plate more effectively than an explosive of low brisance. The Hess and Kast tests for brisance depend on this property, using the deformation of a metal cylinder by the explosive as a measure of the property. In most countries these tests are now little used.

A qualitative test of some value is to fire the explosive standing on its end on a plate of lead about $2 \cdot 5$ cm thick. A strong high velocity explosive

will punch a hole completely through the plate, whereas a weak low velocity explosive will cause merely a minor indentation. This sort of test gives a good empirical indication of the completeness of detonation of the explosive in the unconfined state, provided that it is used along with measurements of power and velocity.

Particular tests are used for nitrocellulose for use in blasting explosives. A typical test is the clearing test, which consists essentially of mixing blasting gelatine under controlled conditions and determining the time at which the explosive is lifted by the stirrers from the bottom of the mixing vessel. This test measures the speed of gelatinisation of the nitrocellulose.

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CHAPTER 7

Permitted Explosives

IN MANY coal mines there is a continual evolution of methane (firedamp) into the air of the workings. The methane is trapped in the coal or rock, often in pockets within the veins, and is sometimes at relatively high pressure. It is usually of fairly high purity, containing only minor amounts of other hydrocarbons and nitrogen. Methane, when mixed with air in proportions between 5 and 14%, forms an explosive mixture. In gassy mines, therefore, there is always the danger that a mixture may be formed which, if ignited, can cause serious damage and loss of life.

In coal mines, also, there is a further danger in that the working of the coal produces coal dust. Coal dust when mixed with air gives a mixture which when suitably ignited can undergo a dust explosion. Indeed, if an explosion of firedamp (or coal dust) occurs, the wave produced can stir the dust lying in the mine into the air, producing a mixture which can lead to further propagation and devastating explosion. In the history of coal mining there have been many examples of both firedamp and coal dust explosions, and the latter in particular have led to serious loss of life.

The firing of explosives in a gassy mine must always be undertaken with suitable consideration of safety. The same is, of course, true of all work, as any electrical fault, or spark from some metals and rock, can give rise to initiation of explosion should firedamp be present in suitable amounts. Most ignitions which occur are local and limited in extent, but there is always the possibility of their spreading to major proportions. The main method of combating this risk is to ensure suitable ventilation so that the firedamp liberated is carried away at a concentration below that at which explosion can occur. Frequent testing of atmospheres, particularly at points where ventilation is less effective than usual, is essential. Stone dusting is used to prevent coal dust explosions. A further and important

measure of safety is the provision of explosives which do not ignite methane/air mixtures under the condition of use. In Great Britain, an explosive for use in gassy mines must pass certain tests carried out by the Safety in Mines Research Establishment at Buxton, as a result of which the Ministry of Power issues the necessary authorisation for use and places the explosive on the Permitted List. Arrangements similar in principle are made in nearly all countries. In Britain the safety achieved is such that ignitions associated with explosives are less than 1 per 10 million shots fired, and are only about a quarter of the total ignitions in coal mines.

Initiation of Firedamp
and Coal Dust Explosions

The high temperature reached in a detonation wave makes it seem improbable that explosives can be designed which do not cause ignition of an explosive mixture of methane and air. The possibility of doing so depends on the very short time for which the mixture is subjected to these temperatures. Methane/air mixtures have a finite induction period and unless energy is applied for at least a considerable proportion of that period, explosion will not result. Deflagrating explosives, such as black-powder, are more dangerous in coal mining conditions than high explosives, because of the much greater time which they take in burning. The strongest high explosives also readily ignite methane/air mixtures, because of their extremely high reaction temperatures. Weaker explosives, but having high speeds of reaction, are relatively safer. Present-day permitted explosives, therefore, always consist of high explosives of which the reaction temperature has been adjusted to a suitably low figure. At the same time care is taken to avoid constituents in the explosive which can continue to burn after the main reaction has been completed, thus setting up in the methane/air mixture a continuing source of ignition.

The mechanisms by which explosives can cause ignition of methane/air mixtures are the following:
1. By direct action of the shock or expansion wave from the explosive.
2. By indirect action of the shock wave after it has been reflected from solid surfaces in the vicinity of the explosion.
3. By ignition of the methane/air mixture on mixing with the hot gaseous products of the explosion.

4. By hot reacting particles of explosive escaping into the methane/air mixture.

It is probable that all of the above mechanisms can operate with certain explosives under some conditions. Strong high velocity explosives suspended in methane/air mixtures cause ignition by the effect of their shock wave. With some high energy explosives, calculations show that the hot gaseous products, when mixed with suitable proportions of methane/air mixtures, can give temperatures and concentrations which lead to gas explosion. Recent studies indicate that explosives can cause centres of initiation of methane/air mixtures at a distance from the exploding charge, and the fact that in many tests the probability of initiation varies according to the shape and size of the containing vessel suggests that shock wave reflections can play an important part. Finally, many workers have shown that reacting particles can penetrate beyond the expanding reaction products of the explosive into the methane/air mixture and can at least assist in causing initiation.

In the practical case, explosives designed for use in coal mines are such that they are unlikely to initiate methane/air explosions by their shock waves when fired inside boreholes. The addition of cooling salts reduces the temperature of the explosion below that at which the gaseous products can cause initiation by thermal effects alone. Therefore only mechanisms (4) and (2) are likely to be of practical importance. Experience shows that initiation by reacting particles of explosive, whilst always possible, is unlikely to be dominant. It is found rather that, in most practical conditions, there is a good correlation between the power developed by the explosive under the actual conditions of firing and the likelihood of initiation of methane/air mixtures. The chance of an explosion therefore depends not only on the explosive, but also on the geometry of the conditions of use, and the safety of a coal mining explosive depends on the operations in the mine for which it is employed.

Research throughout the world has rightly been aimed for many years at the production of explosives incapable of initiating firedamp explosions under any practical conditions. The attainment of such an ideal depends on reducing the effective power of the explosive, so that there are no geometrical arrangements in the coal mine which can cause that explosive to ignite the gas mixture. Such low power unfortunately can only be achieved by limiting the proportion of nitroglycerine and other reactive

ingredients of the explosive to the minimum possible values. As a result the explosives inevitably become less sensitive and less certain in their use. There is an increasing danger that when a number of cartridges are fired in a borehole, particularly when they can be affected by rock movements, some of the cartridges will fail to detonate. These undetonated cartridges can also be liable to deflagrate, that is commence to burn when in the borehole and continue to decompose when the coal or rock is displaced. Such an effect introduces a danger into the coal mine of a different, but still serious, nature. Even if by suitable design of explosive deflagration be avoided, the presence of undetonated cartridges in the product is most undesirable.

It will, therefore, be seen that the best and safest practice is to use in each situation in the coal mine an explosive which is best adapted for the operation in hand. The use of unnecessarily weak explosives, even though apparently safer in some tests, is often a disadvantage and can be dangerous. These considerations have led to the development of a series of types of explosives suited for particular purposes in coal mines and subjected to tests relevant to their individual uses. Thus, in Britain there are now five classes of permitted explosives. In Germany there are three classes. In the U.S.A. geological conditions are different and the hazards are less than in Europe, and it has been possible to work throughout with the strongest types of permissible explosives.

Gallery Testing of Permitted Explosives

It was early recognised that an explosive is more hazardous in a coal mine if it is fired in a borehole from which the stemming is omitted or blown out early by the explosive than if it is fired in a properly stemmed hole and does adequate work in bringing down rock or coal. The tests which led to the original permitted explosives, now called P1 explosives, were therefore designed to test the product under these conditions.

The testing gallery consists of a steel cylinder, 1·5 m in diameter. The first 5·5 m is sealed by a paper or polythene diaphragm and the remaining 9·8 m is left open to the atmosphere. The general arrangmement is shown in Fig. 7.1. At the end opposite the diaphragm there is a hole about 30 cm in diameter against which a heavy cannon is placed. The joint is sealed by

Cannon   Gas explosion   Open end
         chamber
                 Diaphragm
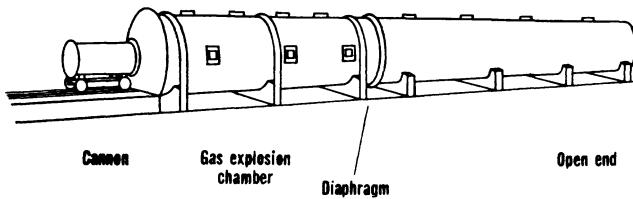
FIG. 7.1. Testing gallery for permitted explosives.

a rubber ring. The cannon is 1·5 m long and has in it a borehole 5·5 cm in diameter and 1·2 m long. The explosive is placed in this borehole with or without stemming according to the test being carried out. After the cannon has been placed in position, methane is introduced into the enclosed portion of the gallery and thoroughly mixed with the air. The explosive is then fired and the ignition, or otherwise, of the methane/air mixture observed from a safe distance.

The results obtained in gallery testing depend appreciably on whether the explosive is stemmed or not and also on the method of initiation. In the British test the stemming used is a close-fitting plug of clay 2·5 cm long. In spite of its short length in comparison with practical stemming, it has a marked effect on the likelihood of ignition of the gas mixture in the gallery. In the original tests, the detonator was inserted last into the cannon and this method of initiation is called direct initiation. If the detonator is at the opposite end of the train of cartridges, and is inserted first into the cannon, the initiation is called inverse or indirect and the probability if ignition of the methane/air mixture is appreciably increased. Figures illustrating this effect have been given by Taylor and Gay and are shown in Fig. 7.2. The same authors have given figures showing how the severity of the test increases as the diameter of the gallery is decreased.

In other countries galleries of similar construction are used, but the dimensions are frequently somewhat different. Data are given in Table 7.1.

Gallery testing in the equipment above is employed for studying the safety of explosives for general applications in coal mines. For explosives for particular purposes special tests have been devised, often to simulate to some extent the hazards which may occur in practice. Typical of these tests are the break tests devised in Britain. These tests are for studying explosives intended for use in ripping, that is in increasing the height of roadways in mines after the coal has been extracted. The extraction of the

coal relieves stresses in the surrounding rocks and is therefore liable to cause breaks which can contain methane/air mixtures. Three tests were devised to indicate the hazard involved in shotfiring in these circumstances.

TABLE 7.1   *Galleries for Testing Coal Mining Explosives*

Country	Gallery		Cannon	
	Diam. (m)	Length[a] (m)	Bore diam. (mm)	Bore length (cm)
Britain	1.5	5.5	55	120
U.S.A.	1.9	6.1	57	55
Germany (Dortmund)	1.8×1.35[b]	5	55	60
Belgium	1.6	5	55	50
France	2	3.5	30	60
Poland	2	3.3	50	70 or 120
U.S.S.R.	1.65	5	55	90

[a] Explosion chamber only.
[b] Elliptical section.
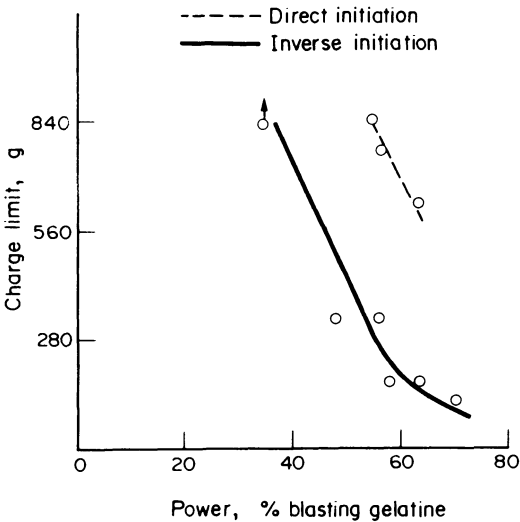
FIG. 7.2. Effect of initiation on gallery testing.

Break 1 test consists of a shothole in which a break occurred across the hole in the middle of the explosive charge. It is simulated by placing a train of explosive across the gap between two steel plates in a test gallery. Break 2 test consists of a break parallel to the shothole and formed in such a way that half the shothole is in one piece of rock and the remainder of the explosive in the space between the rocks. It is simulated by two parallel plates of which the lower one is grooved, the explosive resting in this groove. Break 3 test consists of a break occurring across a shothole, but at the end of the shothole. This is simulated by a cannon fired with the mouth in close proximity to a steel plate. Of these tests, experience has shown that the most severe condition by far is the No. 2 break test and this only will be described in more detail here.
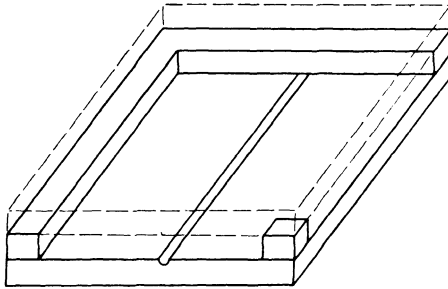
FIG. 7.3. No. 2 break test. (The position of the upper plate is shown by the broken lines.)

The No. 2 break test is shown in Fig. 7.3. Two heavy steel plates 1·8 m square are held either 5 or 15 cm apart. The lower plate has a semi-cylindrical groove of diameter equal to that of a standard borehole. The plates are in a gastight enclosure conveniently formed from steel sides with sheet polythene at the ends and top. The explosive cartridges rest in the groove, as if in a borehole lying in a break. As in gallery testing, the enclosure is filled with an explosive gas mixture. The explosive is fired by a copper detonator and the ignition or otherwise of the gas mixture observed visually.

In the No. 2 break test the explosive is fired almost unconfined. Under these conditions weak coal mining explosives detonate only partially and the probability of ignition of the gas mixture is reduced. Measurement of

power carried out under conditions of poor confinement correlate reasonably well with the likelihood of ignition of methane/air mixtures in the test.
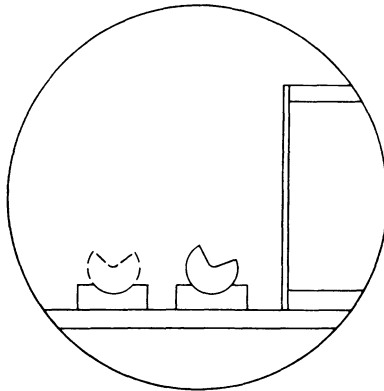
FIG. 7.4. Angle shot mortar.

In other countries other approaches to the study of specially safe coal mining explosives have been employed. Of these, the most popular is the angle shot mortar. This is illustrated in Fig. 7.4. It consists of a heavy cylindrical steel bar with one quadrant removed. The inner angle of this quadrant is rounded to simulate a portion of a shothole. A steel plate is fixed at a predetermined distance and angle from the bar and the whole assembly placed inside a gallery full of methane/air mixture. This test may be considered to simulate a shothole which blows out sideways into a space filled with explosive gas mixture. This test is particularly used in Germany and Belgium.

P1 Explosives

The original permitted explosives are now known as P1 explosives and must pass the following tests:

1. Twenty-six shots are fired of 142 g of explosive with inverse initiation, unstemmed into methane/air mixture. Not more than thirteen ignitions may occur.

2. Five shots are fired of 795 g explosive with direct initiation, stemmed into methane/air mixture. No ignitions may occur.
3. Five shots are fired of 795 g explosive with direct initiation, stemmed into coal dust/air mixture. No ignitions may occur.

In designing P1 explosives, the major consideration is the power. The maximum power of an explosive likely to pass the test depends on the bulk density and Table 7.2 gives approximate figures. Powers exceeding those quoted are liable to cause ignitions in the unstemmed test.

TABLE 7.2   *Maximum Strengths of P1 Explosives*

Type	Density	Max. strength % blasting gelatine
Gelatine	1·5	58
Semi-gelatine	1·25	62
Powder	1·0	66

Ignitions when firing into coal dust suspension are relatively uncommon and appear to depend on the inclusion in the explosive of certain types of ingredients. This effect is, for example, often observed with explosives containing sodium nitrate. For this reason this ingredient is usually avoided and the oxidising agent preferred is ammonium nitrate. To reduce the power to a suitable level, the usual additive is sodium chloride in finely divided form. Typical compositions are quoted in Table 7.3 for Polar Ajax and Polar Viking, gelatine and powder explosives respectively.

P2 Explosives

Lemaire, in Belgium, introduced the concept of enclosing explosives in an inert sheath of cooling material. Most commonly sodium bicarbonate has been used for this purpose. Originally it was packed as a powder round the explosive cartridge and inside an outer paper shell. A further method used in Great Britain was to prepare a "felt" consisting of sodium bicarbonate with a small amount of woodpulp to bind it in usable form; this bicarbonate felt was wrapped round the cartridge of explosive. More recently in Belgium the sheath has been produced as compressed hollow cylinders of sodium bicarbonate into which the explosive is placed.

Sheathed explosives appeared very successful at their introduction, but

Table 7.3   *Compositions of Permitted Explosives[a]*

P1 Explosives

Explosive	NG	NC	AN	Salt	Barytes	Combustible	Other
Gelatine (Polar Ajax)	26·5	0·8	42·7	24·6	—	3·8	1·6
Powder (Polar Viking)	10·5	—	70·7	10	—	8·8	—
Pulsed Infusion (Hydrobel)	40	2	20	27	9·5	1	0·5

P3 Explosives

Explosive	NG	NC	AN	Salt	Combustible	Other
Gelatine (Unigel)	29·2	0·8	25	42·5	2	0·5
Semi-gelatine (Unigex)	16	0·4	46·5	25·5	3·5	8·1
Powder (Unipruf)	8	—	53	29	9·5	0·5

P4 Explosives

Explosive	NG	AN	Amm. chloride	Sod. nitrate	Combustible	Other
Powder (Carrifrax)	9	10	28	46·5	6	0·5

[a] For each composition, official permitted limits are in fact ascribed for each ingredient. The compositions quoted are the mid points of these limits, adjusted to total 100%.

later experience was rather disappointing. There is always the danger of breakage of the sheath and therefore loss of safety. In Britain they have been almost entirely superseded by P3 explosives described below. The tests required for P2 explosives are similar to those for the P3 variety.

P3 Explosives

These explosives, when introduced into Britain, were called "equivalent to sheathed" or Eq.S. explosives. Currently, the explosives must pass the following tests:

1. Twenty-six shots are fired, consisting of 397 g with inverse initiation, unstemmed into methane/air mixture. Not more than thirteen ignitions may occur.
2. Five shots are fired consisting of 1020 g with direct initiation, stemmed into methane/air. No ignitions may occur.
3. Five shots are fired consisting of 567 g with inverse initiation, unstemmed into coal dust/air mixture. No ignitions may occur.

In the design of P3 explosives the first consideration is again that of power. Approximate limits, above which ignition of gas is likely to occur in unstemmed tests, are given in Table 7.4.

TABLE 7.4 *Maximum Strengths of P3 Explosives*

Type	Density	Max. strength % blasting gelatine
Gelatine	1·65	42
Semi-gelatine	1·3	47
Powder	1·0	50

When explosives of the power shown in this table are prepared, the power per unit length of the explosive cartridge is similar to that of the power of a sheathed explosive made from a P1 composition. Effectively, therefore, the difference between a P2 and a P3 explosive is that the inert material in the sheath of the former is distributed uniformly through the explosive composition of the latter. For reasons of stability, however, sodium bicarbonate is no longer used; instead an increase in the proportion of sodium chloride gives the required cooling effect.

In this way P3 explosives of powder or semi-gelatine type can be directly designed. The addition, however, of sodium chloride to a gelatine explosive, in the proportions required, is not possible without loss of the gelatine consistency. In designing a P3 gelatine explosive, therefore, the extra cooling salt is substituted mainly for the oxygen-balanced mixture of

ammonium nitrate and combustible. The development of P3 explosives has been described by Taylor and Gay and typical compositions are given in Table 7.3.

P4 Explosives

P4 explosives were specifically designed for the operation of ripping with delay detonators (see p. 143) and must satisfy the following tests:

1. Twenty-six shots are fired consisting of 397 g inversely initiated, unstemmed into methane/air mixtures. Not more than three ignitions may occur.
2. Five shots are fired of the maximum permitted charge weight of explosive into methane/air mixture in Break test I. No ignitions may occur.
3. Break Test II uses a gas mixture of 3·60% propane with air and nitrogen, which is more easily ignited than methane/air. Preliminary shots determine the most hazardous charge of explosive not exceeding 227 g. Twenty-six shots are then fired at this weight and not more than thirteen ignitions may occur.
4. Five shots of 30·5 cm length and 3·7 cm diameter are fired in methane/air in Break Test III. No ignitions may occur.

In designing P4 explosives, it must be remembered that the overall strength is limited by the requirement of the gallery test, which is even more severe than that employed for P3 explosives. It is, therefore, necessary to include even greater proportions of cooling salts into the explosive than is the case with the P3 class.

Equally severe in practice is the requirement of the break 2 test. To pass this test the explosive must have a low power when fired in an unconfined condition. The actual power has not been quantitatively measured, but is probably in the region of 15% blasting gelatine. To achieve such a result, it is necessary deliberately to design the explosive in such a way that only partial reaction occurs in the unstemmed condition. Such partial reaction can be achieved by either of two ways.

The first method, popular in Britain, consists of adjusting the nature of the ingredients and particularly their specific surface in such a way that the reaction of the oxidiser and combustible is slow. The ingredients are also

such that a flame-quenching solid is released in a form having a high specific surface. For example, in the first explosive of this class, N.E. 1235, much of the ammonium nitrate was introduced in the form of an intimate granular mixture containing calcium carbonate.

In the other method, particularly popular in Germany, the ammonium nitrate is replaced by an equimolar mixture of ammonium chloride and potassium or sodium nitrate. The reaction between the salts, which gives potassium or sodium chloride and ammonium nitrate or its decomposition products, is relatively slow and does not occur to a marked extent when the explosive is fired in an unconfined condition. This method of working is particularly effective in reducing the power of an explosive in the unconfined condition. Used alone it has not proved popular in Britain, because of the low power which tends to be developed under practical firing conditions. Moreover, the finely divided sodium chloride smoke which is produced by the explosive tends to be unpleasant for the miners.

The most recent practice in Britain is to employ a combination of the above methods so as to give the required overall effect on the power of an explosive in an unconfined condition. Compositions and properties of such an explosive are given in Table 7.3.

P5 Explosives

P5 explosives were specifically designed for blasting solid coal with millisecond delay detonators. The nature of this application and its advantages are described in Chapter 14 (see p. 144). In Europe, exchanged ion explosives are used for this purpose. Originally, they gave undetonated cartridges liable to deflagration, but this problem has been overcome by enclosing the cartridges in a plastic sheath and redesigning the explosive to be more powerful. In Britain a consideration of the basic requirements of the explosive has led to an approach in a different direction. It is considered that three special hazards to be overcome relate to ignition of firedamp, desensitisation of the explosive and deflagration.

The particular hazard of firedamp ignition relates to the circumstance when a hole fired early in the round breaks the coal at another hole and exposes the explosive before it detonates. This is simulated by firing gallery tests similar to those described above, but with inverse initiation of a

column of cartridges which reach to 5 cm from the mouth of the cannon. Twenty shots of 567 g explosive are fired into methane/air mixture and no ignitions may occur. The explosive must in addition pass the second and third tests applied to P3 explosives.

Another hazard is that cartridges fired early will cause compression in other holes and thus desensitise the explosive. To overcome this a sensitive explosive is required and one of semi-gelatine type is used in Britain.

Deflagration, or smouldering, is more likely to occur with this technique of off-the-solid blasting than in other methods. This is because coal dust makes deflagration more likely and more dangerous; because there is the tendency noted above towards desensitisation; and because of the high pressures which can be developed in boreholes in view of the good stemming made necessary because blasting is not towards a free face (see p. 138). Deflagration is tested by enclosing two cartridges in a steel tube with controlled venting and with a 10 cm gap between the cartridges filled with coal dust. When one cartridge is detonated the other should not deflagrate if the venting is more than minimal. The nature of the fuel used has a major influence on the liability to deflagration: salts of organic acids are often used. The first P5 explosive (Dynagex) used a special combined fuel and coolant.

P4/5 Explosives

The requirement to use both P4 and P5 explosives in a single mine working leads not only to inconvenience in supply but also to a potential hazard should either explosive be used for the wrong purpose. This has led to the development of P4/5 explosives which pass the tests for both P4 and P5 types and which can therefore be used either for ripping or for firing off the solid with delays.

These are essentially P4 explosives which incorporate the fuels developed for P5 types to avoid the danger of deflagration. When fired off the solid the confinement is sufficient to ensure that the explosive develops its full power and can perform the required work.

Other Coal Mining Explosives

The first successful method of firing explosives in solid coal was the

pulsed infusion technique (see p. 143). This requires explosive which will fire under a pressure of water of 1·4 MPa and which also passes suitable permitted tests, either P1 or P3. Such explosives are based on the addition of high density materials, such as barium sulphate, to a gelatine composition, so as to ensure that it will detonate at high velocity. When this is done propagation under high water pressure can be achieved. By adding appropriate quantities of cooling salts, either P1 or P3 explosives can be designed. The former propagate better under pulsed infusion conditions, whereas the latter enable the shotfirer to use the same explosive for further operations at the coal face. With the introduction of P5 explosives, pulsed infusion techniques are likely to diminish in importance, but they have the advantage of reducing airborne dust and are therefore particularly valuable in anthracite mines.

Mention should be made of devices which are not, strictly speaking, explosives, but which have an explosive effect and can be used for similar purposes in coal mining. Such devices are Airdox, Cardox and Hydrox. All consist of strong metal tubes containing at one end a bursting disc or device of known venting strength. Inside the tube is a cartridge which is caused to liberate high pressure gas at low temperature. When the pressure reaches the designed value the bursting disc breaks and the gas is liberated violently from nozzles at the end of the tube. This sudden liberation of gas causes breaking of the coal. Because of their inconvenience and other disadvantages in operation, these devices are now of limited importance.

References

TAYLOR, J., and GAY, P. F., *British Coal Mining Explosives*. Newnes, London, 1958.
Thorpe's Dictionary of Applied Chemistry, **4,** 558. Longmans Green, London, 4th ed. 1940.

For details of permitted tests, reference should be made to the Health and Safety Executive. For uniformity in text, figures chosen for the above account have been converted to their nearest equivalents in SI units.

Part II.   Blasting Accessories

Introduction

IN EARLY attempts to use nitroglycerine for blasting purposes, the practice was to ignite the nitroglycerine with blackpowder charges. Whilst this caused combustion, it was soon found to be unreliable in producing detonation. Satisfactory results were first achieved by Nobel by the design of the detonator, which employed fulminating substances as ignition compounds. These materials, of a type now called initiating explosives, are characterised by the fact that even in small quantities they detonate on application of flame. Although initiating explosives are sensitive, not only to flame, but also to friction and percussion, they need be made only in such small quantities that special precautions in their handling can be taken. In the course of manufacture, the initiating explosives are enclosed in metal tubes and thereby so protected that the finished product can be handled without danger.

It is always necessary for the shotfirer to be at a distance from the explosive when it is detonated. This can be achieved in either of two ways. The earlier method was to use safety fuse which was ignited at one end and burned slowly towards the detonator, thus giving the shotfirer time to retire to safety. The development of satisfactory and reliable safety fuse was of considerable importance to the explosives industry. But if a large number of shots had to be fired, the operator might not have time to ignite the many ends of safety fuse and still retire to protection before the first explosive detonated. Therefore, a method was sought by which a number of lengths of safety fuse could be ignited by a single operation. This led to the development of igniter cord, which can be joined to the ends of the lengths of safety fuse by special connectors. The shotfirer then only has to ignite one end of igniter cord before retiring.

Although safety fuse is reliable and relatively constant in burning speed, a number of shots fired with this aid will naturally detonate at slightly different times. This can be an advantage, particularly if the times of detonation are varied by altering the length of safety fuse, or by ensuring

suitable delays by the use of igniter cord. On other occasions, however, it is desirable to be able to fire a number of shots simultaneously. For this purpose detonating fuse can be employed by which ignition is caused by a detonation wave instead of burning. A detonation wave in the fuse travels at 6500 m s^{-1} so that a larger number of shots can be fired almost simultaneously. The detonating fuse itself must be initiated by a detonator, but can be used without further attachments for initiating most nitroglycerine explosives. For less sensitive explosives such as slurries the detonating fuse can be used to initiate a primer or booster of a cast explosive such as pentolite.

The alternative method of ensuring safety for the shotfirer is to enable him to fire the round of shots from a safe distance by using electrical means. For this purpose electric detonators have been developed. An electric detonator is placed in each shothole, the leads are connected into a single electrical circuit and the whole fired from a central point. The original electric detonators did not allow use to be made of the advantages described in Chapter 14, of firing shotholes in a prearranged order in time. This led to the development of delay detonators, which are electric detonators incorporating delay elements. When an electric current is passed through delay detonators they are actuated immediately, but the base charges do not detonate till after prearranged times. The first delay detonators manufactured had intervals of either 1 or 0·5 s, but more recently delays of the order of 30 to 50 ms have been produced and are in wide use.

The above represent accessories which do not directly perform blasting operations, but which are essential for the efficient and safe use of blasting explosives. For the explosives industry and for the user they are as important as the blasting explosives themselves.

CHAPTER 8

Initiating Explosives

Mercury Fulminate

Mercury fulminate has the formula $Hg(ONC)_2$. It was probably discovered by Howard in 1800 and its constitution was established by Nef. The method of preparation is known as the Chandelon process and is a complex reaction studied by Wieland. Mercury is dissolved in an excess of warm nitric acid and ethyl alcohol added to the resulting solution. Considerable bubbling occurs in the strong reaction, so this is usually carried out in capacious glass "balloons". At the end of the reaction the mercury fulminate remains as a dense precipitate which is filtered and washed several times.

Mercury fulminate is a pale brownish solid, insoluble in cold water, but dissolving slightly in hot water to a solution which does not give the normal mercury reactions. In cold conditions it is stable, but at higher temperatures gradually decomposes and loses strength as an explosive. It has a density of $4 \cdot 45$ g ml^{-1} and a velocity of detonation, when compressed to a practical density of $2 \cdot 5$, of about 3600 m s^{-1}.

When used in detonators, mercury fulminate is frequently mixed with 10 or 20% of potassium chlorate. Such mixtures have a better oxygen balance and therefore give improved and more reliable initiation of other explosives.

Lead Azide

Lead azide, discovered by Curtius in 1891, has the formula $Pb(N_3)_2$. Hydrazoic acid, HN_3, is a liquid boiling at 37°C and because of its sensitiveness is an extremely dangerous substance. As a strong acid it

gives salts with many metals and these can range from stable compounds such as sodium azide to very sensitive solids such as the copper and silver azides. The starting point in azide manufacture is sodium azide, itself made from sodamide and nitrous oxide. Sodium azide is one of the few soluble azides and therefore the salts of other metals can readily be prepared by precipitation in aqueous solution.

Lead azide is manufactured by reaction of sodium azide with either lead nitrate or lead acetate. It is a white crystalline solid, insoluble in cold water and stable on storage. It is very sensitive to friction and impact and has a velocity of detonation, when pressed to a density of $3 \cdot 8$, of 4500 m s^{-1}.

Two crystallographic forms of lead azide are important, the ordinary alpha form which is orthorhombic and the beta form which is monoclinic. The densities of these forms are $4 \cdot 71$ and $4 \cdot 93$ respectively. It was for many years believed that the beta form is the more sensitive to friction and impact and accounted for detonations which have occurred in the manufacture and handling of the substance. It is now known that the beta form is in fact no more sensitive than the alpha. Even the alpha form, when present as large crystals, is very sensitive and conditions can arise (particularly when the formation of the lead azide is controlled by diffusion effects) where spontaneous detonation occurs. Although with modern knowledge these hazards can be avoided, pure lead azide is nevertheless a dangerous compound and is now made only for military purposes.

Commercially, lead azide is usually manufactured by precipitation in the presence of dextrine, which considerably modifies the crystalline nature of the product. The procedure adopted is to add a solution of dextrine to the reaction vessel, often with a proportion of the lead nitrate or lead acetate required in the reaction. The bulk solutions of lead nitrate and of sodium azide are, for safety reasons, usually in vessels on the opposite sides of a blast barrier. They are run into the reaction vessel at a controlled rate, the whole process being conducted remotely under conditions of safety for the operator. When precipitation is complete, the stirring is stopped and the precipitate allowed to settle; the mother liquor is then decanted. The precipitate is washed several times with water until pure. The product contains about 95% lead azide and consists of rounded granules composed of small lead azide crystals; it is as safe as most initiating explosives and can readily be handled with due care.

Lead azide has virtually supplanted mercury fulminate in the

manufacture of commercial detonators, having better storage properties under hot conditions and also greater initiating power for base charges. Lead azide does, however, suffer from two disadvantages. One is its ready reaction under moist conditions with copper, or copper salts. The second is its relative insensitiveness to initiation by flame, such as the spit of a safety fuse.

Many other methods of making lead azide in a safe form have been described, but the only one to have found commercial importance consists of replacing the dextrine by a small proportion of gelatine. When properly made this form of lead azide is as safe to handle as the dextrinated form and has improved sensitiveness to flame. It can therefore be used by itself in electric and delay detonators, but not in plain detonators as it is not ignited with certainty by safety fuse.

Lead Styphnate (Lead 2, 4, 6-Trinitroresorcinate)

This compound has the formula $(NO_2)_3C_6HO_2Pb$, but usually contains also one molecule of water as water of crystallisation. Trinitroresorcinol is manufactured by the nitration of resorcinol and is then usually converted to the magnesium salt, which is reacted with lead nitrate solution under warm conditions and with good stirring. The product is precipitated as a red crystalline material which can be washed by decantation and separated by filtration.

Lead styphnate is a poor initiating explosive which when dry is very sensitive to friction and impact, to electrostatic discharge, and to flame. Its main use is as an additive to lead azide to improve flame sensitiveness (see p. 101). When pressed to a density of $2 \cdot 6$ g ml^{-1} it has a velocity of detonation of 4900 m s^{-1}.

Diazodinitrophenol (DDNP, DINOL)

This substance has the following formula:
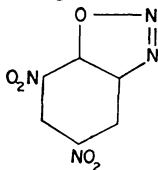
Originally prepared in 1858 by Griess, it is made by diazotising picramic acid with sodium nitrite and hydrochloric acid according to the following reaction:
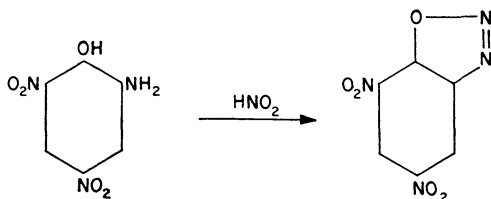
Diazodinitrophenol is a yellow powder, almost insoluble in cold water. It does not detonate when unconfined, but when confined has a velocity of 6900 m s^{-1} and a density of 1·58 g ml^{-1}. For an initiating explosive it is relatively insensitive to friction and impact, but still is powerful when confined. DDNP has good properties of storage and has found application in detonators, particularly in the U.S.A.

Tetrazene

This compound has the following formula:
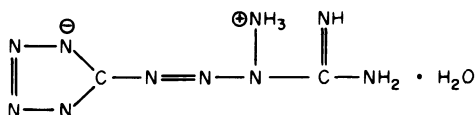
Tetrazene was discovered by Hofmann and Roth in 1910 and the structure determined by Duke. It is made by the action of sodium nitrite on aminoguanidine sulphate or nitrate under slightly acid conditions.

Tetrazene is a light yellow crystalline substance, insoluble in water and most organic solvents. The density is low under normal conditions, but on pressing can reach approximately 1 g ml^{-1}. Tetrazene is weak as an initiating explosive, and is therefore not used alone. It has no advantages to commend it for use in commercial detonators, but does find application in the manufacture of military and other percussion caps. Like diazodinitrophenol, tetrazene does not detonate when ignited in the open, but only when ignited under confinement.

Reference

Thorpe's Dictionary of Applied Chemistry, **4**, 558. Longmans Green, London, 4th ed. 1940.

CHAPTER 9

Plain Detonators

A PLAIN detonator consists of a metal tube, closed at one end and containing an explosive charge of which at least a part is an initiating explosive. The normal use is for firing in conjunction with safety fuse. The main factors governing detonator design are safety, stability on storage, certainty of ignition and initiating power.

Safety

Initiating explosives are sensitive to friction and impact so that the safety of the device must be provided by the detonator tube. For this reason tubes are invariably made of metal and proposals to use plastic have met with no success. The tubes used have a diameter of approximately 6 mm, this being a convenient size for insertion into a cartridge of blasting explosive. With a wall thickness of about 0·3 mm, such tubes are adequately strong for purposes of both manufacture and use. The safety achieved is often remarkable; indeed, occasions have occurred when detonators have been completely flattened by being run over by vehicles without exploding. Such safety cannot, however, be relied upon, and in particular any friction inside a detonator from inserted hard objects is extremely dangerous.

Metal cups are sometimes inserted in detonators to provide extra confinement for the composition. It is often claimed that such cups, by increasing the mechanical strength, also increase the safety of handling of the detonator. In the case of plain detonators this is true to a limited extent, but the difference is not of practical importance. Of much greater importance is the ensurance of the absence of grit or hard particles, the presence of which can cause dangerous sensitiveness in the detonator.

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Stability on Storage

Detonators must be capable of storage for long periods under various types of climate. After such storage the detonators should still be in safe condition and also perform normally.

The original initiating explosive used by Nobel and all manufacturers for many years was mercury fulminate. This had the disadvantage of decomposing slowly in hot climates, particularly under moist conditions. For this reason mercury fulminate is no longer widely used. In most countries it has been replaced by a mixture of dextrinated lead azide and lead styphnate. In the U.S.A. some detonators are made containing diazodinitrophenol.

The introduction of lead azide led to a difficulty in the choice of metal for the detonator tube. Under moist conditions, lead azide and copper can react to form cuprous azide on the inner wall of the tube and thus in a particularly dangerous position. Therefore with plain detonators, which cannot be sealed, copper cannot be used when lead azide is employed. Such detonators are usually made from aluminium tubes, or occasionally zinc.

Certainty of Ignition

The initiating explosive used must ignite with certainty from the spit of a safety fuse. It must be remembered that the intensity of the spit can be reduced if the safety fuse is not cut squarely and also that the fuse may in practice not always be fully inserted into the detonator. Lead azide by itself is not sufficiently easily ignited to give a satisfactory plain detonator and it is therefore used in admixture with lead styphnate, which is very readily ignited by flame. The proportions of such mixtures vary from 25 to 50% of lead styphnate. Mercury fulminate and diazodinitrophenol are sufficiently sensitive to flame not to require such additives.

Although the requirement for flame sensitiveness is the main consideration for initiating explosives for plain detonators, others are important in manufacture. The explosive must be capable of compression into a coherent mass and at the same time leave the equipment free from adhesions. Lead azide can be somewhat deficient in cohesion, and to improve this a small proportion of tetryl is sometimes added to the

mixture. In Britain, but not in other countries, it is common practice to add a small proportion of fine flake aluminium to the mixture, the purpose being to improve lubrication in the presses and to prevent adhesion to the punches.

Initiating Power

To some extent detonators and blasting explosives are designed together so that one will initiate the other with certainty. Experience with fulminate detonators showed that the No. 6 detonator containing 1 g of a mixture containing 80% mercury fulminate and 20% potassium chlorate could reliably initiate the nitroglycerine and TNT explosives in use. Such a detonator can be considered the normal minimum strength in most countries. Changes in design have, however, led to an overall increase in strength so that the No. 6 detonators now being sold are in fact more powerful than the original.

For both technical and economic reasons, current detonators contain a base charge of high explosive which provides the main initiating power of the device. The most satisfactory high explosives for use as base charges are PETN, tetryl and RDX, and of these the first is by far the commonest, because of its sensitiveness and relatively low cost.

The strength of the detonator depends to a large extent on the weight of base charge employed, but for a given weight of base charge the strength may be increased by the following measures:

1. Increasing the pressing of the base charge to give a higher density. This leads to a higher velocity of detonation and therefore greater initiating power.
2. Use of a narrower diameter tube. This leads to a longer length of base charge which in general is more effective in initiating blasting explosives.
3. Increasing the thickness of the metal of the tube. Within limits this gives greater confinement and therefore more effective detonation of the base charge.

In practice detonators of increased strength are made by increasing the weight of the base charge rather than by other means. The only important exception to this is the German Briska detonator (see p. 103).

Construction of Plain Detonators

The general construction of a British plain detonator is shown in Fig. 9.1; other countries in general adopt similar designs.
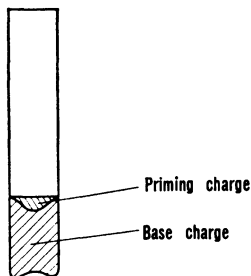
FIG. 9.1. Plain detonator.

The tube is of aluminium, 6·4 mm external diameter and with an overall length of 35 mm; the wall thickness is 0·3 mm. The base is dimpled inwards, as this construction gives a miniature cone charge and therefore a somewhat increased initiating power at the end of the detonator (see p. 158). These tubes are made from aluminium sheet by drawing into cups, annealing and then drawing by several stages to the final size. After drawing, the tubes are trimmed to length to give a neat open end. The tube length is designed to give an unoccupied space of approximately 2·5 cm in the finished detonator. In use the safety fuse is inserted into this portion of the tube, which is then crimped round the fuse to hold the assembly together.

The base charge consists of PETN and the No. 6 detonator contains 0·24 g. The charge is pressed at 28 MPa, this pressure being chosen to give adequate density and velocity of detonation without imposing undue strain on the tube with any liability of causing splitting. By use of a flat, or dimpled, punch, the surface of the base charge can be produced either flat or with a conical depression. The latter construction gives advantages in the initiation of the base charge, but by blocking of punches can give rise to more frequent faults in manufacture.

In Briska-type detonators the base charge is loaded in two portions. The first is pressed at about 140 MPa, the tubes being specially supported. The second addition is pressed to a normal pressure and serves to initiate the more highly compressed explosive. In Britain it is preferred to increase detonator strength by increasing the weight of charge; thus the strongest

commercial detonator (No. 8 Star) contains 0·8 g **PETN** in a tube of slightly increased diameter.

The normal initiating charge in a British detonator is lead azide modified with gelatine. In the case of plain detonators a small proportion of lead styphnate is added to the azide to ensure satisfactory ignition from safety fuse.

Manufacture

The tubes after manufacture are examined for any faults and then loaded, open end uppermost, in holes of a carrying plate, usually 181 at a time. The plate is first placed in a charging machine for PETN. This machine has a charging plate with 181 holes of standard size. It rests on a base plate, also with 181 holes, but initially displaced from these holes by finite horizontal distance. A charging hopper containing PETN is moved backwards and forwards across the charging plate until the holes are full. The plate is then slid until the holes coincide with those of the base plate, so that the PETN in measured volume drops through into the detonator tubes. The charging plate is then removed and placed under a press with 181 punches, where the base charge is consolidated.

The ingredients for the priming composition are dried separately under carefully controlled conditions. They are then weighed and carefully mixed behind blast protection, usually in a simple conical cloth bag. The mixing may be facilitated by adding a number of rubber balls. The mixture is then passed through a coarse sieve, still by remote control, into bags for transport to the loading unit.

The charging of the detonators with priming composition is carried out by a method similar to that used for the base charge, although the quantities involved are smaller and the volumes added similarly small. Again after charging, the charging plate is taken to a press where the priming charge is compressed to a total load of about 15 tonnes. Both charging and pressing of the priming composition must be carried out under full remote control.

The detonators as made may be dirty, that is have free priming composition as a dust on the walls. They are therefore transferred to a drum containing a quantity of dry sawdust. The drum is rotated for a

predetermined time and the detonators then removed and shaken free of sawdust. In this way any free priming composition is removed and also any loose charges would be broken down. The detonators are then carefully inspected and finally packed. Most detonators in Britain are now made on fully automatic equipment. The physical principles are the same except that the final removal of loose priming composition is by vacuum cleaning.

Testing of Detonators

The essential property of a detonator is its initiating power, but this is very difficult to measure. The best type of test is carried out by manufacturing a series of explosives of decreasing sensitiveness and attempting to initiate them with the detonator under examination. The first of these tests is known as the Esop test and employs picric acid as a standard explosive, gradually diluted with olive oil as a means of reducing sensitiveness, but the results depend critically on the grist of the picric acid. A rather more reproducible test has been based on milled TNT ammonium nitrate explosives desensitised with salt. A standard range of such explosives is used, and for each composition the sensitiveness can be further varied by pressing the explosive to a varying extent. In tests of this sort it is important to assess the detonation of the high explosive by indentation of a lead plate or by a lead crusher. Tests of the type described here are tedious to carry out and also give results which depend to some extent on the nature of the high explosive used.

For routine testing simpler tests can be employed. One such uses a lead plate 0.5 cm thick and resting on an iron support with a circular hole of radius 18 mm. The detonator is fired when standing vertically on the plate above the centre of the hole and in contact. The dent or hole in the lead plate is compared with a series of standard deformations from detonators of increasing strengths. This test measures only the end blow of the detonators, whereas in initiating explosives the side blow can be at least as important. Another test commonly used is to fire a detonator lying on a standard iron nail and observing the bending produced in the nail. Such a test can give a rough indication of the side blow of the detonator. All tests of this sort should be used only for comparing constancy of manufacture

in a single type of detonator. Their use in comparing detonators of different constructions can be grossly misleading.

Reference

MARSHALL, A., *Explosives Vol. 2, Properties and Tests.* Churchill, London, 2nd ed. 1917.

CHAPTER 10

Electric Detonators

ELECTRIC detonators consist of plain detonators to which a device has been added for generating a flash on receipt of an electric impulse. The first devices of this sort were invented by Watson in England and Benjamin Franklin in the U.S.A. and utilised electric sparks for igniting gunpowder charges. The modern method of igniting a flashing composition by passing the electric current through a fine wire was invented by Hair in 1832. Suitable ignition systems were therefore available long before detonators themselves were invented.

It is convenient to distinguish four systems by which the electrical energy can be converted into a flash.

1. A bridge of resistance wire is connected across the ends of two leading wires and surrounded by a loose charge of flashing composition or of initiating explosive.
2. A bridgewire similarly attached to the ends of leading wires is coated with a coherent layer or layers of flashing materials.
3. The leading wires are attached to a fusehead, originally a separate entity and containing a bridgewire surrounded by coatings of flashing composition.
4. The leading wires are again attached to a fusehead, but this contains no resistance wire, having a flashing composition which is itself made sufficiently conducting to ignite when a high voltage is placed across it.

The construction of these types is shown in Fig. 10.1 (p. 108).

Type 4 gives a high tension detonator, so called because it requires at least 36 volts to fire it. The electrical conductivity is achieved by adding graphite to the flashing composition, but control of electrical properties is difficult and the finished product liable to change on mechanical handling or on storage. For this reason detonators of this type are no longer employed.

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Detonators of the first three types all employ bridgewires and therefore require low voltages for their initiation. The choice is one of manufacturing convenience, but as most makers prefer type 3, only this will be described in detail.
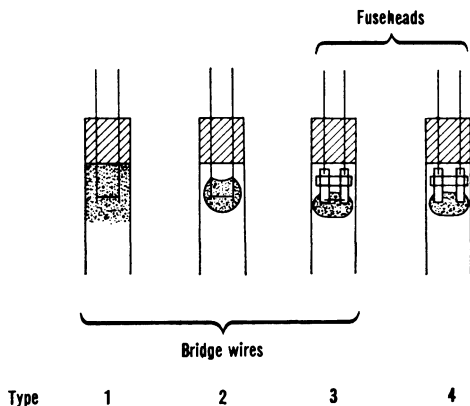
FIG. 10.1. Types of detonator ignition systems.

The flashing device, without leading wires, is known as a fusehead and its construction and properties will be considered first.

Fuseheads

The first successful type of fusehead was invented by Krannichfeldt in Germany. This "sandwich" type of construction is used in many countries, including Great Britain, and is illustrated in Fig. 10.2.

The manufacture of a sandwich fusehead proceeds in the following manner. Brass or other metal foils are fixed on each side of a sheet of pressboard with a suitable adhesive. The pressboard is then stamped into combs of the shape shown in Fig. 10.3 and steps are cut in the tips of the heads. Fine resistance wire is stretched across the heads and soldered to the foil on each side of the pressboard. These operations were originally all carried out by hand; now many are carried out mechanically.

A number of these combs are fixed side by side with spacers in a carrying plate. The tips of the combs are then dipped into a solution of paint-like consistency containing flashing compositions to be described
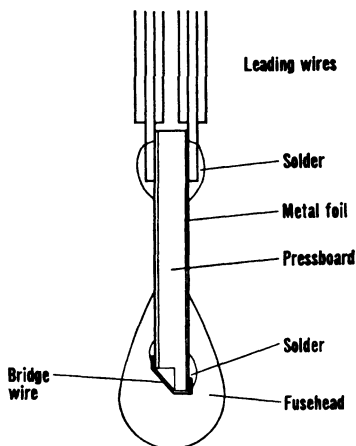
FIG. 10.2. Sandwich fusehead.

later. A series of dips is given with drying between each stage. The combs are then removed, cut into individual fuseheads and at the same time tested for suitability of resistance.

FIG. 10.3. Fusehead comb.

An alternative design of fusehead much used in Europe is known as the Unifoil fusehead, invented by Schaffler. The principle of the production of modern fuseheads of this type is shown in Fig. 10.4. A metal strip, usually of steel, is first stamped as shown at *A*. A band of plastic is then moulded as shown at *B*. Further stamping produces pole pieces as at *C*, the ends of which are first bent upwards and then clinched over resistance wire which is introduced into the angle formed. The bridgewire is then welded to the pole pieces. Excess plastic and wire is removed and the combs thus formed are dipped in the same manner as described for sandwich type fuseheads. After dipping, the individual fuseheads can be removed and tested. In the original Schaffler design the foil was tinned on one side so that the bridgewire could be soldered in place rather than welded. The plastic described was not used, but the pole pieces were instead held in place by insulated metal clips. Both types of fusehead are currently made.
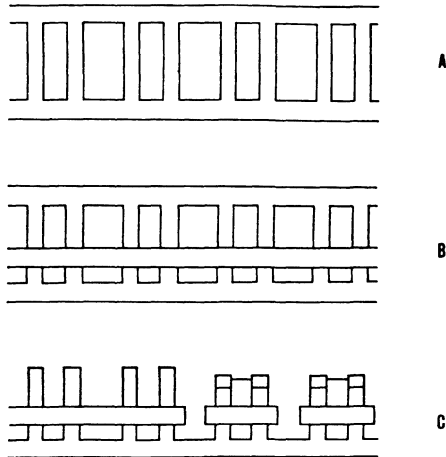
FIG. 10.4. Unifoil fusehead manufacture.

The properties of a fusehead depend very largely on the bridgewire employed. The energy liberated per unit length of wire is proportional to I^2r, where I is the current applied and r the resistance. If ignition is to occur in a finite time, commonly of the order of 50 ms, the quantity of heat evolved from the bridgewire must exceed a minimum which depends on the nature of the flashing composition. If the fusehead is to fire with a suitably low current, for example 0·5 A, a bridgewire of high resistance per unit length must be employed. Suitable high resistances can be achieved by using nickel chromium alloys in gauges of about 48 S.W.G. For fuseheads to be fired with a different current the bridgewire can be made of other materials, or of other diameters.

The first dip given to a fusehead is known as the flashing composition and is of particular importance. Originally copper acetylide was used for this purpose, but it has been superseded by more stable materials. Three common compositions are based on lead picrate, lead mononitroresorcinate and a mixture of charcoal and potassium chlorate respectively. These materials are suspended in a solution of nitrocellulose in amyl acetate and amyl alcohol, known as Zapon. One or more dips, with intermediate drying, give a layer of suitable thickness.

The second dip, or series of dips, is intended to provide a suitable flame which can ignite the initiating explosive in the detonator. These dips are commonly based on potassium chlorate and charcoal, again suspended in

Zapon. The fusehead is finally given a coat of a nitrocellulose solution as a protective layer and this coat may well be coloured with pigment so that the type of fusehead can readily be identified.

Assembly of Electric Detonators

Leading wires are made from tinned iron or copper, of gauges from 23 to 25 S.W.G. They are insulated with plastic, commonly PVC, coloured to enable different types of detonator to be readily distinguished. Two such wires are wound, usually by machine, to form figure eight coils of total lengths ranging from $1 \cdot 2$ to $5 \cdot 5$ m, according to requirements. The coils are held together by a few turns of the two leading wires around the bundle. The four ends of wires are stripped of insulation to a suitable distance.
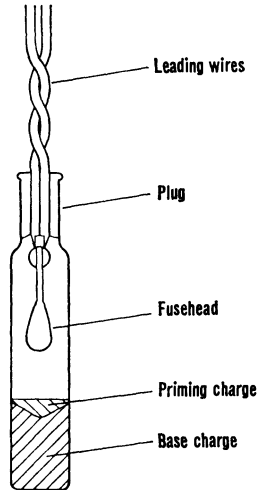
FIG. 10.5. Electric detonator.

A small cylindrical plug is fixed near one end of the leading wires, either by threading on a pre-formed plug, or by moulding plastic around the wires at a suitable point. The bared ends of the wires immediately adjacent to the plug are then soldered to the two conducting foils of the fusehead. In the case of Unifoil fuseheads the wires are soldered or welded to the metal tags. The completed assembly is then inserted to the correct depth inside a plain detonator and the tube crimped round the plug to hold the detonator

together and to provide a watertight seal. The structure of the completed detonator is shown in section in Fig. 10.5.

For detonators to be used where electrostatic charges may occur, it is desirable to prevent sparking from the fusehead to the case, should a high voltage be generated on the leading wires. For this purpose, an insulating sheath is inserted, either into the detonator tube or else immediately around the fusehead.

Electric detonators are made from aluminium or copper tubes, the latter being for use in coal mines where aluminium may lead to a possibility of ignition of methane/air mixtures.

Firing Characteristics of Electric Detonators

When an electric current is passed through a fusehead, the sequence of events shown in Fig. 10.6 occurs. After a time known as the excitation time, the fusehead ignites and this may or may not cause rupture of the bridgewire. The time it takes for the bridgewire to be broken is known as the lag time and this may equal the excitation time, or be as long as the
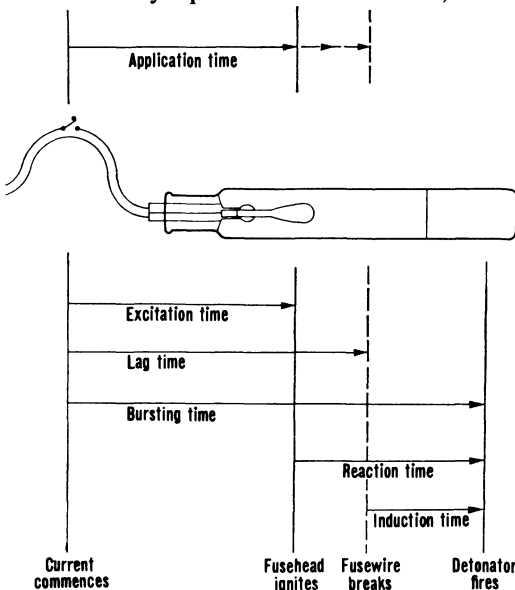
FIG. 10.6. Sequence of events in firing electric detonators.

bursting time, which is the time between the application of current and the explosion of the detonator. The interval between the ignition of the fusehead and the bursting of the detonator is known as the reaction time and the interval between the breaking of the fuse wire and the bursting of the detonator is known as the induction time.

For any particular kind of fusehead these times depend on the magnitude of the electric current applied. If a steady current, less than the minimum firing current of the fusehead, is applied, the bridgewire does not get hot enough to ignite the flashing dip, so that the fusehead remains un-affected. As the magnitude of the current is increased, the fusehead ignites with gradually reduced excitation times and therefore with gradual reduction in overall bursting time. In applications where short bursting times are essential, as in seismographic work, not only are special detonators used, but the firing currents employed are maintained as high as possible.

Although steady currents are sometimes applied to fire detonators, it is equally common to use exploders which have a finite time of current application. This may be either incidental, because the mechanism is the discharge of a charged condenser, or deliberate in the case of coal mining applications where finite time of pulse is desirable for safety reasons. Such finite pulse times, usually of the order of 4 to 5 ms, prevent the possibility of later sparking between leading wires, etc., in the presence of methane/air mixtures. When a pulse of current is used to fire a detonator, the time for which it is applied is known as the application time. If the detonator is to be fired successfully, the magnitude of the current must be such that the application time of the exploder exceeds the corresponding excitation time of the fusehead.

When a large number of shots are to be fired it is common practice to connect the electric detonators in series and fire them all with the single application of an exploder. The current from the exploder ceases when the first fuse wire breaks and therefore at the time of the shortest lag time of the detonators involved. This time will depend on the magnitude of the firing current, as shown in Fig. 10.7. In this figure the curve *A* represents the minimum lag time shown by any detonator in a large number selected from those made to a single specification. Owing to minor variations in in-gredients, etc., during manufacture, the average lag time will be at each point longer than that shown on the curve. Also shown in Fig. ·10.7 in curve *C* is the maximum excitation time characteristic of the fuseheads in-

volved. Again because of random variations during manufacture, the average excitation time will be less than that shown in the curve. For any single fusehead, of course, the excitation time cannot exceed the lag time. If a number of fuseheads in series is to be fired successfully, the shortest lag time of the fuseheads involved, which determines the application time, must exceed the longest excitation time present in the circuit. This is the case in Fig. 10.7 for currents greater than those corresponding to point Y where the two curves cross. Point Y is therefore the minimum series firing current, which is in all cases greater than the ordinary minimum firing current for a single fusehead.
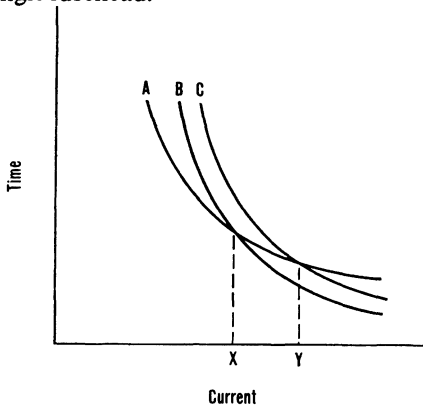
A : Minimum lag time

B : Minimum excitation time

C : Maximum excitation time

X : Minimum firing current for single detonator

Y : Minimum series firing current

FIG. 10.7. Series firing of electric detonators.

The curves of Fig. 10.7 apply only to fuseheads made to the same specification. If fuseheads are made with different bridgewires or different flashing dips, the corresponding curves could be completely different and there may be no point at which the minimum lag time of one type of detonator exceeds the maximum excitation time of the other. Under these conditions series firing would not be practicable and it follows that it is not feasible to use different types of detonators in a single series firing circuit.

CHAPTER 11

Delay Detonators

Introduction

As is discussed in Chapter 14, it is often advantageous if a number of detonators are fired not simultaneously but in a predetermined order. With ordinary electric detonators, such sequential firing can be achieved only by the use of complicated wiring circuits and of special switches attached to the exploder. These disadvantages are overcome by the use of electric delay detonators. In delay detonators a time lag is deliberately introduced between the firing of the fusehead and the explosion of the detonator. If a number of such detonators are fired in series the fuseheads all ignite simultaneously, but the detonators fire at predetermined intervals depending on the construction of the delay detonators. Only a single wiring circuit and single exploder is needed to carry out the actual firing operation.

The earliest delay detonators were introduced in Great Britain in 1910 and had a length of safety fuse between the fusehead and the detonator proper. The construction is shown in Fig. 11.1. The fusehead was sealed in a paper tube by a sulphur plug and this tube in turn sealed into a metal sleeve. The other end of the sleeve was crimped onto safety fuse and the free end of the safety fuse crimped into a detonator. An important part of the construction of such a detonator is the presence of a small hole in the metal sleeve, usually covered initially with adhesive tape. The firing of the fusehead and the safety fuse punctures the adhesive tape and the hole then provides a vent from which the hot gases can escape without an increase in pressure sufficient to cause too rapid burning of the safety fuse. The emission of hot gases which is essential with this structure of detonator is a serious disadvantage in practice as it can lead to premature ignition of the primer of high explosive. For this reason, and because of relative

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inaccuracy in delay times, this type of delay detonator is now only rarely used.

A real advance in the construction of delay detonators was made by Eschbach, who introduced delay compositions which evolved so little gas that there was no longer need to vent the detonator. This eliminated risk of pre-ignition of high explosive and also made it possible to provide fully waterproofed assemblies which gave delay times much more regular because of the removal of variable venting effects. Delay detonators of this type have now virtually superseded all others.

Waterproofing   Vent   Rubberised tape

Sulphur   Fusehead   Safety fuse   Detonating explosive
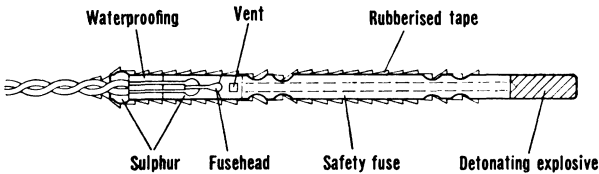
(a) Early vented delay detonator

Neoprene plug   Fusehead   Delay   Priming   Base
                                      element   charge   charge
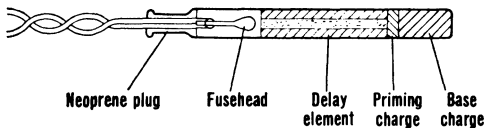
(b) Modern delay detonator

FIG. 11.1. Construction of delay detonators.

Gasless delay detonators are manufactured to fire after pre-arranged delay times, each manufacturer providing a series of detonators with intervals of usually 1 s or 0.5 s. More recently a further type of delay detonator has been introduced, usually known as the millisecond, or short delay detonator. Again, manufacturers provide a series of fixed delay times, but in this case the interval between each number of the series is much shorter and may be from 25 to 50 ms.

Delay Compositions

The mixtures used in providing delay elements contain an easily oxidised element, often a finely divided metal, together with an oxy-salt or an easily reduced metal oxide. The first of such mixtures to attain wide use was that employed by Eschbach and consisted of a mixture of elemental antimony and potassium permanganate. When such a mixture is ignited, the antimony is oxidised to antimony oxide and the potassium permanganate reduced either to the manganate or to a mixture of potassium and manganese oxides, depending on the proportions present. Whilst a little gas is formed in a side reaction of permanganate decomposition, the amount is small and the pressure developed inside a detonator is not large. The reaction products form a solid slag of indeterminate composition. The proportions commonly used vary from 55 to 70% of permanganate with 45–30% of antimony.

In the U.S.A. a common mixture for delay elements consists of selenium and barium peroxide which reacts to give selenium oxides and barium oxide. Usual proportions are 85% of barium peroxide with 15% of selenium.

For the manufacture of millisecond delay detonators, faster burning compositions are necessary. Many have been suggested, but the two most commonly used are based on silicon mixed with either red lead or lead dioxide. Typical mixtures would contain between 30 and 50% of silicon and the remainder as oxidising material.

The burning of a column of delay composition takes place by the passage of a reaction front along the column. The temperature profile of this reaction front can be measured by the use of suitable thermocouples and recording instruments. By analysing the shape of the front it can be shown that the reaction is a solid/solid reaction initiated by thermal conduction of heat through the unreacted material. It follows that to obtain reproducible reaction rates there must be (1) constant amount of solid to solid contact and (2) constant thermal conductivity.

To attain adequate surface contact between the reacting solids it is necessary to use the ingredients in fine condition and to bring them into contact by pressure. To maintain both solid contact and thermal conductivity correct, the density of the column is controlled at a uniform value. The manufacture of satisfactory delay compositions, therefore, entails the provision of suitably sized ingredients followed by adequate mixing and accurate pressing.

Manufacture of Delay Elements

Delay compositions are not normally pressed direct into detonator shells because of the irregular delay times which result from the relatively low compression thus possible. Instead they are made into delay elements by either of two basic methods. The more general method comprises pressing into brass or aluminium tubes which are a sliding fit into the detonator shell and which are thick enough in the wall to withstand heavy consolidating pressures. The other method consists of filling a lead tube with the delay composition and drawing it down in diameter by conventional means. This process gives a length of lead tube filled with delay composition ready for cutting into the required lengths. The process of drawing itself consolidates the delay composition.

For either method, the delay composition must be made in a free-flowing form. In the case of the antimony/potassium permanganate mixtures, this is done by mixing fine antimony and fine potassium permanganate and then pelleting the mixture in a press. The pellets are then broken down and after sieving to remove fines a suitable free flowing granule is obtained. For other types of compositions this method is not generally applicable because of the difficulty of forming pellets by pressure. Instead the mixture is granulated with a small amount of nitrocellulose solution by working in a suitable mixer.

The actual filling of brass or aluminium delay elements is similar in principle to the filling of plain detonators described above. The loading is, however, carried out in a number of stages so as to ensure uniformity of density of the column throughout its length.

The manufacture of lead elements commences with the filling of a lead tube, probably 1 m long, by tamping in delay composition. This tube is gradually drawn down until it is of the correct external diameter to be a sliding fit into the detonator shell. It is then accurately cut to the lengths required to give the delay times.

Assembly of Delay Detonators

Assembly commences with a plain detonator containing its base charge and initiating explosive. These detonators are held in plates and the processes are insertion of suitable delay elements, followed by pressing in the normal way. They are then checked by X-ray examination to ensure

proper assembly. A fusehead, complete with plug and leading wires, is placed in position in each detonator and crimped to give the finished product.

Design of Delay Detonators

Some special points of design may be noted. Thus, some delay compositions, particularly antimony/potassium permanganate mixtures, have relatively poor igniting powers for initiating explosives. This can be controlled by suitable design of the delay elements, or alternatively, an intermediate layer of priming explosive of high sensitiveness, such as lead styphnate, can be introduced between the element and the lead azide charge. Another point to be watched is the possibility of "flash past", particularly in the shorter delay periods where the lengths of the elements used are at a minimum. In the past it has sometimes been the custom to introduce a layer of delay composition above the initiating explosive before placing in the delay element. Nowadays, however, improved overall design and technique has made this unnecessary.

Some delay compositions are difficult to ignite and ordinary fuseheads may not be adequate for this purpose. In such cases special fuseheads are used which commonly contain cerium powder, or some similar additive which burns with the evolution of a large amount of heat.

In the design of the detonator attention must also be paid to the effects of the liberation of gas which, though small, is still sufficient to require attention. As the speed of the delay composition is affected by pressure, it is necessary that the free space in the detonator should be carefully controlled. Also, the plug which seals the leading wires in place must withstand this pressure for more than the delay period of the detonator. This task is made more difficult by conduction, along the metal walls of the detonator shell, of heat liberated by the fusehead and the delay composition. Plastic plugs in particular are liable to soften and be ejected from the detonator with probable failure of burning of the delay column.

Delay detonators for use in coal mines must be constructed so as not to ignite methane/air mixtures even if fired accidentally outside a cartridge of a blasting explosive. This requires a suitable selection of fusehead and the provision of the delay element in a form which will not produce large particles of hot slag on burning. In the British design the delay elements are

of the lead type, but with five or six narrow cores instead of the single central column. Such "Carrick" detonators will satisfy even the rigorous British test, which involves firing the detonators in a simulated break, formed by two steel plates 5 to 15 cm apart and filled with methane/air mixture.

Detonating Fuse

Introduction

A detonating fuse is a narrow cord of explosive which is capable of detonating from one end to the other at high velocity and therefore of transmitting detonation almost instantaneously from one cartridge to another some distance away. The thinness of detonating fuse makes it essential to use explosives which are capable of propagating reliably at such small diameters. The earliest fuses of this sort were made with either dry nitrocellulose or more commonly with mercury fulminate phlegmatised with wax. Such fuses were irregular and dangerous in use as they were sensitive to initiation by shock. The first successful detonating fuse was Cordeau, which was made in the following manner. TNT was cast into a lead tube and allowed to solidify. The whole tube was then drawn down to a diameter of 4 mm. This drawing process at the same time broke down the cast TNT and brought it into a sensitive form which would propagate whilst still confined by the lead tube. Cordeau had a uniform velocity of detonation of about 5000 m s^{-1} and was also safe to handle.

From about 1930 onwards a new type of detonating fuse appeared on the market. This consisted of a core of PETN with textile and plastic coatings. Compared with Cordeau, this detonating fuse has several advantages in being more flexible, more easily jointed, lighter in weight and cheaper to manufacture. Under such names as Cordtex and Primacord it has completely replaced Cordeau in normal use.

Detonating fuse is made by either a dry process or a wet process. The former is generally more popular because of its lower costs for ordinary types of fuse. The latter is, however, used particularly in North America.

Manufacture by the Dry Process

The PETN must be sufficiently fine to propagate reliably in small diameter; at the same time it must be relatively free flowing. These two properties are to some extent contradictory, but suitable grades can be manufactured by careful attention to the method of precipitating the PETN during purification.

The PETN is placed in a hopper with a conical base leading to an orifice. This is shown schematically in Fig. 12.1. A centre cord of textile, usually cotton, passes down through the hopper and assists the flow of the PETN.
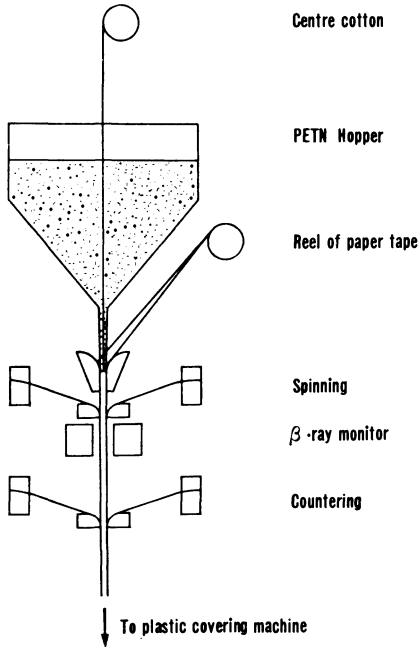
FIG. 12.1. Principle of dry process for detonating fuse.

Immediately below the nozzle a tube is formed from a strip of paper which is bent round in a forming die. The paper tube thus formed and containing relatively loose PETN passes through a second die, at which stage it is also spun with textile, often in this case jute to give maximum tensile strength. This second die is smaller than the first and therefore exerts a consolidating

effect on the core of the fuse. The fuse is finally countered and covered with plastic by extrusion.

In any process for manufacturing detonating fuse it is important to ascertain that there are no gaps in the PETN core. Such gaps would cause failure of the fuse to propagate detonation. A test is therefore done, either with a roller diameter detector or by beta-ray monitor to determine the presence of the core. The roller diameter detector consists of two spring-loaded rollers which approach each other in the absence of a core and indicate the fault. A beta-ray monitor determines the total weight of matter in the fuse by measuring its beta-ray absorption. Any lack of a core then is indicated in an alarm or other device. The fuse is also examined at various stages of manufacture for flaws in textile or plastic covering.

Manufacture of Detonating Fuse
by the Wet Process

The PETN used in the wet process is finer than that required for the dry process. It is no longer required to flow freely in the solid dry condition, but is suspended to a fluid paste in water with a suspending agent. This paste is then braided with textile fibre and dried in a continuous drier. The remaining stages in the process consist of countering with textile, covering with plastic and possibly final braiding. The speed of operation is determined by the rate of drying of the PETN paste and is therefore slower than that of the dry process where the limiting speed is usually the operation of the countering machinery.

Properties of Detonating Fuse

The velocity of detonation of a fuse is about 6500 m s^{-1}. This is attained in the dry process by adequate consolidation of the core during manufacture. During the wet process the necessary density is attained automatically by the method of preparing the core. Fuse usually contains about 10 g PETN per metre length.

A satisfactory fuse must be capable of propagating laterally from one line to another. In this way it is practicable to join lengths of fuse by ordinary knots, such as the reef knot. In test, the usual method is to lay two strands of fuse at a measured distance apart and ascertain that one

initiates the other. The gaps necessary for satisfactory use are small and in the region of 6 mm. Alternatively, the test can be for propagation between fuses separated by varied thicknesses of card.

The tensile strength of the fuse is of some importance, as it is common practice to lower charges down a large hole by means of the detonating fuse. A strength of 35 kg is adequate, but higher strengths can be achieved when necessary by the addition of further amounts of textile.

Further properties which a detonating fuse should have are the ability to initiate blasting explosives (tested with suitable relatively insensitive mixtures usually of TNT and ammonium nitrate); resistance to low temperatures without cracking on flexing and to hot storage without desensitisation; and toughness to prevent damage from stones, etc. The fuse must always be waterproof and must often withstand diesel oil, which can separate from ANFO.

Low Energy Detonating Cord (LEDC)

When detonating cord is not required directly to initiate high explosives, but solely to transmit detonation from one place to another, it is sometimes an advantage to use a cord with a very low charge weight. Two types of such cord are at present available in certain countries.

The first type to be introduced consisted of PETN or RDX in a metal sheath drawn down to a small diameter. More recently, cord made by the wet process, covered with plastic instead of metal, has been introduced in North America and is available in charges down to 0.6 g m^{-1}. The methods of manufacture of these cords are believed to be similar to that of Cordeau and the wet detonating fuse process described above.

When used for laying above ground for connecting shots in civil engineering, quarrying, etc., a low energy detonating cord has the advantage of producing much less noise than the normal grade. This avoids any requirement of covering the cord with earth or sand when used in populous areas. Another use for the cord, particularly the plastic variety, is in connection with blasting with ANFO. The cord itself has insufficient initiating power to cause ANFO to detonate and can be attached to a special delay detonator. In this way propagation between holes by detonating fuse can be achieved with the extra advantage of the introduction of suitable delay times between individual holes. The

particular advantage of this method with ANFO is the absence of electric fuses and therefore complete safety in dry conditions where static electricity may be generated. Special connectors must be used if LEDC is to be joined to ordinary detonating fuse.

Nonel

As the loading density of a powdered solid explosive is reduced the detonation velocity becomes less. This follows from equation (5) of Chapter 2, as p_2 is smaller the lower the density. Calculation shows that at the lowest densities the detonation velocity tends towards a limiting lower value, typically about 2000 m s^{-1}. This is also the detonation velocity in a dust explosion of these substances.

Nonel fuse, invented by Nitro Nobel AB in Sweden, consists of a thick plastic tube of bore about 1 mm, the inside surface of which is dusted with a small amount of powdered high explosive. If a shock wave is formed at one end of the tube the explosive powder is raised to a dust and a stable detonation at velocity 2000 m s^{-1} proceeds indefinitely along the fuse. The plastic itself is unaffected and the only outside effect is a flash of light seen through the tube walls. This therefore is an extremely safe method of propagating a detonation from one place to another.

In practice lengths of fuse are supplied sealed in the factory to prevent ingress of dust or moisture. The detonation may be started in various ways such as a small detonator or by firing a blank cartridge. At the other end of the fuse the flash is sufficient to ignite the priming explosive of a plain detonator or the delay element of a delay detonator. Plastic mouldings are available so that branch lines may be introduced. It is therefore possible to fire from one point any number of detonators in any predetermined delay sequence. The system is very simple to operate and is immune to stray electric currents in the ground due to electric circuits or lightning discharges.

Safety Fuse

WHEN blackpowder was used for blasting, the original method of initiating the charge was by means of a straw or goose quill filled with loose blackpowder, and ignited with paper or string coated with blackpowder paste. Such initiation was irregular and caused many accidents. In 1831 William Bickford introduced safety fuse which consists of a core of blackpowder enclosed in textile sheaths and suitably waterproofed. Regularity of burning is of extreme importance and in Great Britain the fuse must burn within set limits, 87 to 109 s m^{-1}. It must also not emit any side sparks during burning, nor be capable of igniting similar fuses placed alongside it.

Manufacture

Safety fuse is made from fine grain blackpowder, although certain processes use mill cake, or indeed blackpowder ingredients themselves. The normal process is illustrated further in Fig. 13.1.

Blackpowder (fuse powder) is fed down a tube from a safety loft into a spinning die, usually made of hardened steel or tungsten carbide. At the same time, centre cottons pass down with the blackpowder so. as to maintain adequate flow. Also introduced into the spinning die are the spinning yarns of jute, the purpose of which is to enclose the blackpowder core for later processing. This processing consists of consolidation by passing through further dies of smaller diameter and then countering in textile yarns, usually jute.

The semi-fuse thus produced is waterproofed by passing through troughs of molten bitumen or by coating also with plastic.For higher grade safety fuse, a further countering of textile, such as cotton, is followed by a final varnish, which may be coloured for identification purposes.

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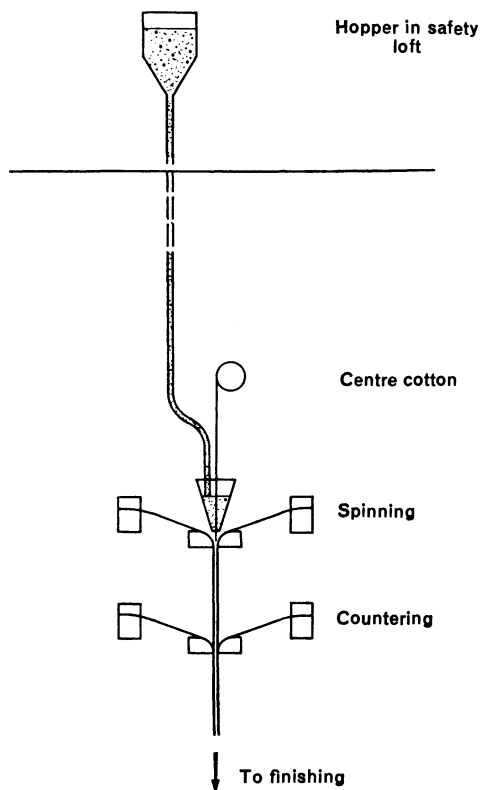
FIG. 13.1. Principle of safety fuse manufacture.

To obtain the best results, the fuse powder should have a relatively low potassium nitrate content, and a typical formula would be

Potassium nitrate	65%
Sulphur	24%
Charcoal	11%

Such a powder gives less smoke than the 75% nitrate composition and eliminates side sparking.

During manufacture it is important that the fuse should not be allowed to stand in the molten bitumen, or the core may be penetrated. The time for such faults to develop depends on the construction of the fuse, and is shorter the lower the potassium nitrate content of the powder and the

thinner the covering of textile provided by the spinning and countering yarns.

To maintain regularity of burning speed it is essential that high quality fuse powder is employed. It is normal to determine the quality from samples before use and this is conveniently done by filling the powder into a lead tube, which is then rolled down to a small diameter. The regularity of burning of the lead fuse is then determined. If a high-grade powder is employed, then regularity of burning of the finished fuse may be secured provided that sufficient attention is paid to giving regular confinement by control of the construction of the envelope.

Safety fuse covered only with bitumen can be used with care in dry conditions but normal practice requires better protection from rough handling and moisture. For many years this was given by gutta percha and textiles but the former material is no longer readily available. Coatings of plastic such as polyethylene are now used. Early products had the disadvantage of speeding up in burning under water and causing irregularity of firing of shotholes under wet conditions. This defect has been removed by careful design. Current fuses therefore have excellent resistance not only to abrasion and water but also to the fuel oil in ANFO.

In the Fritzsche process blackpowder is not employed, but only the mixed ingredients of potassium nitrate, sulphur and charcoal. These are fed into the process by special methods, but the final construction and use of the fuse remain unchanged.

Properties of Safety Fuse

As the blackpowder core of a safety fuse burns, it produces gases which must escape. At the same time the heat of the combustion melts the bitumen and plastic and thus produces side venting through the textile layers. This results in the production of an increased but constant gas pressure, determined by the equilibrium between gas generation and gas lost sideways. As the rate of burning of blackpowder depends markedly on the pressure, it is this process of equilibration which determines the speed of burning of the fuse.

With a properly constructed safety fuse the core is almost impermeable to gases, but should faults occur, either during manufacture or due to mishandling afterwards, cracks may develop which enable the hot gases to

penetrate forward. In this case the speed of the burning of the safety fuse can increase and even become violent.

It follows also that the actual rate of burning of safety fuse depends on the ambient pressure. Indeed, if the pressure is reduced to less than about a fifth of an atmosphere the burning ceases altogether. In deep mines the extra pressure can be sufficient to give an increase in burning speed of safety fuse. Compared with the effect of pressure other influences on the burning speed are small. Temperature has little effect and humidity also has little effect unless the fuse is kept for a prolonged period at a humidity sufficient to cause deliquescence of the potassium nitrate in the core.

The gas evolved by safety fuse consists mainly of carbon dioxide and nitrogen with some carbon monoxide and oxides of nitrogen. The amount of gas produced is likely to be 15 to 20 ml per cm of fuse.

Testing of Safety Fuse

Because of the extreme importance of regularity and freedom from failure which must characterise safety fuse, detailed and exhaustive tests must be carried out on the product. Certain controls are obvious, namely, measurement of powder charge and of burning speed, both before and after immersion in water. Other tests usually carried out include resistance to cracking on flexing at low temperatures round a mandrel, "coil" tests in which the fuse is bunched into flat or complex coils and freedom from failure after immersion in water is determined. New types of fuse are usually tested to indicate the amount of smoke produced and also to determine the adequacy of the end spit. The end spit is the projection of particles of burning powder from a cut end and is of importance because it provides the mechanism which enables the fuse to ignite a detonator.

Instantaneous Fuse

For some purposes, particularly in fireworks, instantaneous or almost instantaneous transmission of flame is required without detonation such as is characteristic of detonating fuse. Instantaneous fuse is used for this purpose, deliberate use being made of one of the possible faults in safety fuse, namely, the rapid speeding up which can occur if the core of the safety fuse is porous.

Instantaneous fuse consists of a highly combustible thread, often made from nitrated paper, inside a tube of known diameter. The nitrated paper occupies only a small part of the cross section of the tube, so that the gases can penetrate along it freely. The high speed of burning is caused by the rapid passage of hot gases along the tube, igniting the core well in front of the portion already consumed. The rate of burning is not easily controlled, but the uses to which the fuse is put are such that this is not of great importance. Threads coated with blackpowder may be used in place of a nitrated paper core. Instantaneous fuse is usually made only in small quantities by simple hand methods.

Igniter Cord

If the outer covers of safety fuse are pierced, e.g. by falling rock, water can penetrate and stop the combustion of the fuse. Much work has been done in efforts to obtain a waterproof fuse which will obviate this difficulty. This work, although not successful in its original purpose, has led to the development of igniter cord which has proved of considerable value in secondary blasting (see p. 148). Two types of igniter cord are manufactured, fast cord with a burning speed of 3 s m^{-1} and slow cord with a speed of 30 s m^{-1}.

In the manufacture of fast cord the first process is to coat paper or textile yarns with a blackpowder/nitrocellulose dope by a dipping process. These yarns are thoroughly dried and a number of them passed through an extruder and given a thick covering of plastic incendiary composition. The cord thus produced is covered with a protective layer of plastic, usually polyethylene. The overall diameter of the cord is about 2·5 mm.

The speed of burning of fast igniter cord depends on the speed of burning of the blackpowder-coated yarns and this depends in turn on the gas channels left in the construction of the fuse. The remainder of the fuse is also combustible, so that there is no pressure build up due to lack of venting. Should a minor pin hole or break in the outside layers be produced and water enter, the incendiary composition will continue to burn so that the fuse will not fail, although it will slow down for the distance of the damage.

Slow igniter cord consists of the same type of plastic incendiary composition extruded not over combustible blackpowder-coated yarns,

but over a metallic wire. The function of the wire is to conduct heat from the burning front into unburnt composition and so control and speed up the rate of burning of the igniter cord. This centre is usually of copper, but may be of iron or aluminium. Slow igniter cord is covered with a thin layer of protective plastic.

The basis of igniter cords is the incendiary plastic. Of the possible compositions those which have achieved most importance are based on a nitrocellulose binder with oxidising and combustible additives. The nitrocellulose is normally plasticised with dibutylphthalate and contains also the usual stabilisers. A low viscosity lacquer grade of nitrocellulose is most conveniently employed. The oxidising components consist of a balanced mixture of red lead with either potassium nitrate or potassium perchlorate. The addition of a potassium salt is found to give certainty of pick up of flame and suitable vigour in combustion, but its quantity is restricted by the requirement that the finished product should be safe under conditions of impact such as can occur in use. The combustible additive is usually finely divided silicon. The incendiary composition is thermoplastic and extruded hot. In bulk it can burn vigorously and therefore special safety precautions are required in processing, including automatic guillotines to cut the fuse at suitable points in case of fire.

Igniter cord is used for the purpose of igniting a number of lengths of safety fuse at predetermined intervals. Special connectors are therefore supplied for transmitting the flame from the igniter cord to the safety fuse. The connector consists of an aluminium tube, closed at one end, into which a pellet of incendiary composition is pressed. An elliptical "bean hole" is then cut through the two sides of the tube and the composition. In use, the connector is crimped to the cut end of safety fuse; the igniter cord is then bent double and the doubled portion passed through the bean hole, which is crimped firmly with a special tool. The side flame from the igniter cord sets fire to the incendiary composition in the connector and this in turn ignites the safety fuse. Some designs of connector contain also blackpowder to assist propagation of the flame, but such connectors are generally employed only when supplied from the factory already fastened to lengths of safety fuse so that there is no danger of penetration of moisture to the blackpowder during storage.

Part III.   Application of High Explosives

Commercial Applications

Introduction

The major applications of blasting explosives are in mining and quarrying, where the purpose is to break solid rock into smaller fragments. In the British Isles the most important operation is coal mining, for which permitted explosives are almost entirely employed. Other underground mining is for gypsum, anhydrite, non-ferrous metal ores, iron ore and to a small extent rock salt. Surface uses include opencast (strip) coal mining, quarrying and civil engineering work such as is encountered in hydroelectric schemes and road building. In all these cases the general procedure is to drill a hole into the solid rock or coal, insert cartridges of explosives with a detonator and thereby use the explosives to fracture and bring down the rock. The nature of this process has been studied in some detail, particularly by Livingston, Langefors and Hino.

The first effect of the firing of an explosive in a borehole is the production in the surrounding rock of a shock wave, either directly from the explosive in contact with the rock, or by the impact on the rock of the expanding detonation products. This shock wave produces in the rock both compressive and shearing forces, the former being by far the most important. The compressive forces themselves are unable to break rock, but when they reach a free surface, or a fissure in the structure, they are reflected as rarefaction waves. The stages of this reflection process are shown in Fig. 14.1 for various time intervals. It will be seen that at the free surface and immediately adjacent to it the rarefaction and compression waves compensate each other. At a distance from the free surface the rarefaction wave can exceed the compression wave at a suitable instant of time and the net stress can exceed the tensile strength of the rock. When this happens the rock is fractured and fragments break off. In a perfectly uniform material this can happen only at the outside surface and the effect

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is to produce a spalling of a surface layer. In heterogeneous materials such as ordinary rocks, reflections can occur at other points and fissures are produced at a wide range of places throughout the mass.
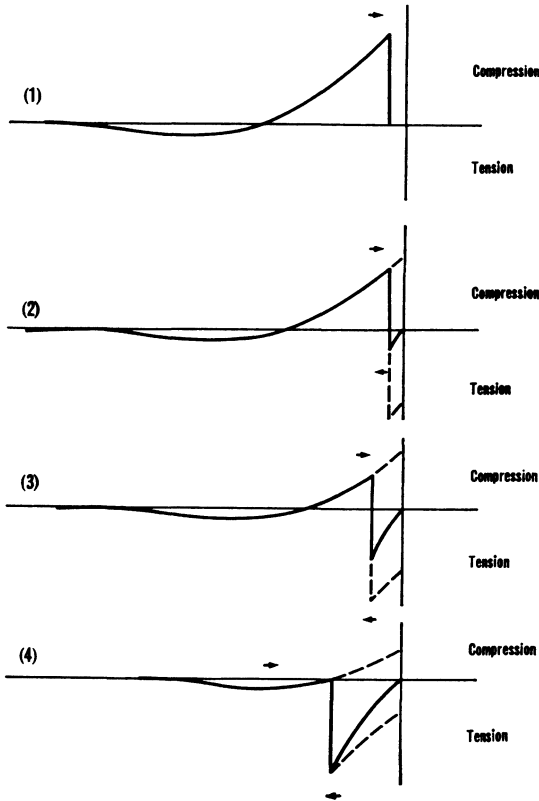
FIG. 14.1. Stages in the reflection of a shock wave at a free surface.

After the shock wave has passed through the rock the borehole still contains hot gases at high pressure. As there are now fissures in the rock, however, the strength is reduced to a negligible amount and the gases can expand and throw the broken rock away from the solid mass.

If the amount of explosive used is too large, the broken rock can be projected for great distances. If the quantity used is too small, the amount of fissuring of the rock can be insufficient to free the explosive gases

adequately and these are then most likely to blow the stemming from the borehole, but to leave the mass of the rock intact. In a properly balanced explosive shot the rock is broken into fragments, but the expansion of the gases causes only sufficient movement to move these fragments a short convenient distance. Many factors influence the optimum charging rate for boreholes, and skill and experience of the shotfirer are of considerable importance in attaining optimum effects.

x Indicates initial position of explosive
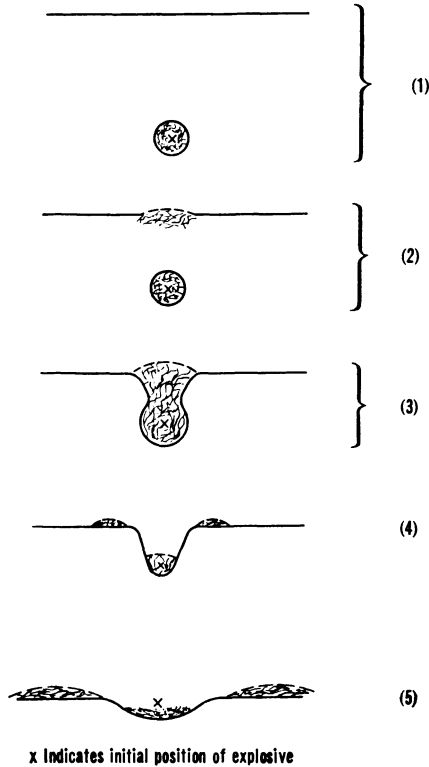
FIG. 14.2. Effect of depth of charge on cratering.

The efficiency of an explosive in any given rock can be determined by cratering experiments. In these, boreholes are drilled vertically downwards into the rock and loaded with increasing charges of explosive. The effects which are produced are shown in Fig. 14.2. The optimum charge produces

a crater extending to the bottom of the borehole, but does not project the broken rock so far that most of it cannot fall back into the crater originally produced. By utilising the results of such trials, it is possible by mathematical formulae and by experience to estimate accurately the charges needed in practical mining and other operations.

It will be seen that the reflection of the shock wave from a free face is of considerable importance in the use of explosives. In practice, the most economic use of an explosive can only be achieved if it is fired at a suitable distance from such a free face. This distance is known as the burden of the shot. If, as in tunnelling, no free face exists naturally, the first shots fired are heavily loaded and arranged so as to produce such a free face for the later charges.

Tunnelling

As an illustration of practical methods of using explosives it is proposed to describe in some detail the way in which a tunnel may be driven through rock. This is a process common to all mining operations and frequently used in hydroelectric and civil engineering work.

The principle employed is to drive a number of boreholes into the rock, load them with explosive and fire the explosive. This is known as drilling, charging and firing the round. The broken rock is cleared away and the length of the tunnel has then been increased by approximately the depth of drilling the boreholes. The length by which the tunnel is increased by each cycle of operations is known as the advance. As the tunnel advances, its inner surface is made smooth and secure by lining with steel and concrete, or other means.

The boreholes may be drilled in many patterns, differing essentially in the arrangement by which the first section of rock is removed and a free face developed. A method which is applicable under most circumstances is known as the wedge cut and this is illustrated in Fig. 14.3 for a medium-sized tunnel. In Fig. 14.3 the boreholes are shown in elevation and section; the figures in brackets refer to the period of delay of the detonator used in each individual hole.

In approximately the centre of the line of the tunnel, but usually somewhat below this, there is a series of six holes, three on each side, arranged in the form of a wedge. These are drilled at an angle so as to be

inclined towards each other and almost meet at the back of the holes. These six holes are fired simultaneously with detonators containing no delay elements.
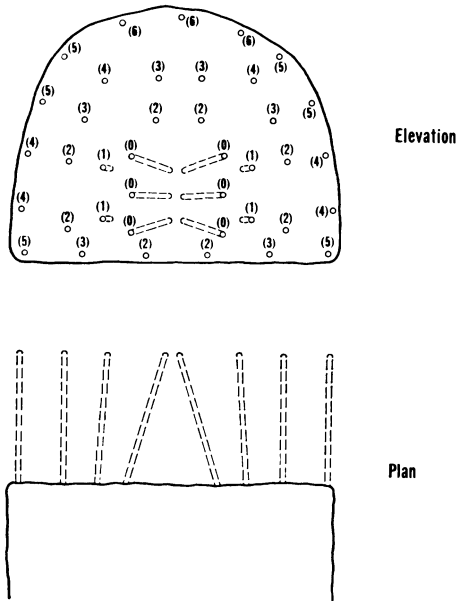
Fɪɢ. 14.3. Wedge cut.

Around the wedge are drilled a number of holes known as easers, arranged in approximately concentric rings. The detonators used in these holes have delays which gradually increase in number as the hole is farther from the wedge. This is to ensure that the inner holes nearest the free face always fire first and can produce a fresh free face against which the farther shots can work. Finally, an outer row of holes, known as trimmers, are drilled close to the intended outline of the tunnel. The trimmers have the longest delays, particularly at the top of the tunnel.

The sequence which occurs on firing is that the rock in the wedge is first blown out and then the hole thus produced is expanded outwards as each successive ring of charges detonates. Apart from the first six holes, which in any case are angled suitably, the explosives in the other boreholes all work towards a free face.

In an operation of this sort, the commonest explosive used is an ammonium nitrate gelatine such as Polar Ammon Gelignite. The wedge holes are likely to contain about 1 kg each of explosive and the other holes less than half this amount. The appropriate charge is usually calculated according to the nature of the rock, varying from 1 to 4 kg per m³ of rock between the softest and the hardest strata.

The charges in the boreholes are made up of a number of cartridges, paper wrapped, each containing 110, 170 or 230 g of explosive. One of these cartridges is made into the "primer" cartridge by the insertion of a detonator. The first operation is to insert a soft metal pricker into the end of the cartridge so as to make a hole for the detonator. The detonator is then inserted firmly and completely into this hole. It is important to ensure that the detonator is not pulled out of the cartridge during subsequent operations, and a convenient way of doing this is to tie the leading wire of the detonator round the cartridge with a half hitch. The cartridges of explosives are placed in the borehole and pushed firmly but gently home with the help of a wooden or brass-tipped rod, known as a stemming rod. The primer cartridge can be inserted first or last, but always with the base of the detonator pointing towards the main length of the charge as this is the direction in which initiation is best. When all the explosive is in, the hole is stemmed by the insertion of clay, sand or similar material so as to
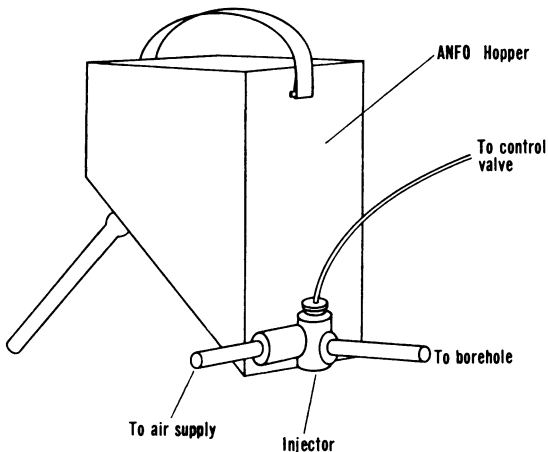
FIG. 14.4. "Anoloder" for ANFO.

provide a resistance against the explosive when the latter is fired. This stemming is packed tightly with the stemming rod.

When all the holes have been charged, the leading wires from each detonator are separated and connected together with the detonators in series. The two free ends of the circuit are then connected to the shotfiring cable, the continuity tested and the round fired when all the personnel are in safe places.

When ANFO is used underground it is loaded into the hole by means of compressed air. The equipment used for this purpose can be of two types illustrated in Figs. 14.4 and 14.5. Figure 14.4 shows an injector loader of which the best known is the "Anoloder". This consists essentially of a hopper at the base of which is an injector similar to a steam injector, but using compressed air which follows the external annulus, allowing the ammonium nitrate/oil mixture to pass through the central portion. The mixture of ANFO and air is carried through a hose into the borehole. The other type, shown in Fig. 14.5, is known as the blow case and in this
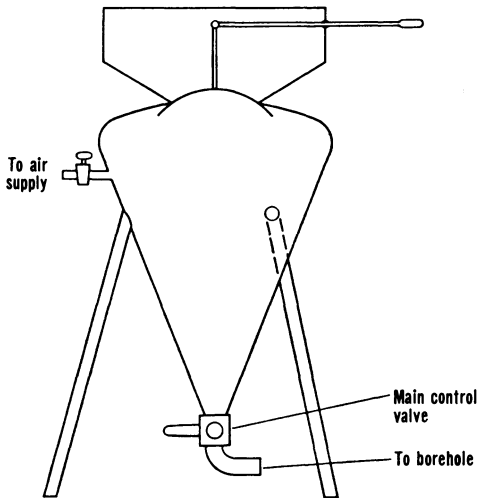
FIG. 14.5. Blow case loader for ANFO.

design the container is sealed and pressurised with compressed air. This blows the ANFO out through the bottom of the container, through a hose and into the borehole. When ANFO is used the primer is usually inserted

last to allow time for dispersal of any static electrical charges caused by the loading of the hole.

Coal Mining

In order to describe the uses of explosives in coal mining, it is first necessary to give a brief outline of the method of mining usually adopted in the British Isles. This is known as the long wall system.

Before mining commences, shafts are driven from the surface to the required depth. At least two shafts are required for ventilation to be possible. From these shafts, tunnels called stone drifts are made, roughly horizontally, to the coal seams. The seams may be 1 m or more thick and are usually inclined at an angle to the horizontal.

The actual work of getting coal is at a long straight face of 100 to 200 m in length. At each end of this face is a road which is used for conveying coal and materials and also for ventilation. The mining process consists of extracting the coal along the whole length of the face to give a regular daily advance. The first stage in extraction is known as undercutting and consists of cutting a 10 or 12 cm slot to a depth of about 1·5 m. This creates a free face to which the explosives can work. Shotholes are drilled near to the roof level and filled with the explosive and fired. This breaks the coal down so that it can be loaded onto conveyors which pass along the face to the road. In mechanised mines this whole operation of obtaining coal is done by machine.

As the face advances, the two roads must be similarly brought forward. Indeed, with mechanised mining, there is at each end of the face a "stable hole" somewhat in advance of the face, so that the machinery can be positioned between the cuts. Further, in many pits the thickness of the coal may not be as high as that of the roads, namely, 3 m or so, so that the roads are enlarged as they advance by a process known as ripping.

It must be remembered that methane can be liberated in a coal mine, not only in the coal itself, but in the nearby stone. It is therefore necessary to use permitted explosives, both in and near a seam of coal. Further, before any shot is fired in a coal mine, tests are made for the presence of methane in the air by means of a safety lamp. This safety lamp is the well-known Davy lamp and an experienced operator can judge the presence of methane in the air from the appearance of the flame. Tests are made

particularly near the roof where methane can accumulate, being lighter than air. As a precaution against coal dust explosions, the neighbourhood in the mine is sprinkled liberally with limestone dust which has the property of suppressing these explosions.

Explosives are used in coal mines for a wide variety of purposes. For example, in the initial sinking of shafts P1 explosives of the gelatine type are frequently employed. In making the roadways, similar explosives can be used following the principles described above in tunnelling. The other place in coal mines where explosives are fired in stone is in the process of ripping. This in principle is a simple application to bring down stone above an existing opening. The particular situation in the mine is, however, unusually dangerous and high concentrations of methane are liable to occur in this vicinity. At the same time, for speed of operation the use of millisecond delay detonators is desirable. As the bottom of the rock is unsupported, separation of the rock is liable to occur, either before shotfiring or between the succession of shots. These small partings, known as breaks, can contain methane and then give rise to exceptional hazards in firing. To meet this situation, the P4 class of explosives has been introduced into Britain. These are specially tested for safety when fired in the presence of breaks containing methane/air mixtures (see p. 86).

Explosives are fired in coal on the face, in the stable holes and sometimes in the making of roads. The commonest practice, as stated above, is to undercut the coal mechanically. Often a single row of holes with a permitted P3 explosive is then sufficient to bring down the coal. Powder explosives are most commonly used for this purpose, water-proofed when necessary.

The process of undercutting is time consuming and also requires machinery in a congested part of the mine. It is also one which produces a large amount of dust and adds to ventilation difficulties. It is therefore natural that means have been sought of avoiding undercutting. Historically, the first was the use of pulsed infusion shotfiring, illustrated in Fig. 14.6. A special explosive (see p. 89) which will fire when subjected to a high pressure of water is placed at the back of the borehole. In the front of the borehole is placed a seal to which a water infusion tube is connected. Water is pumped through this tube until it is at the desired pressure and the whole of the borehole full of water. When the explosive is fired it is in fact surrounded by water and this considerably reduces the risk of gas ignition and also the amount of dust and fume set free.
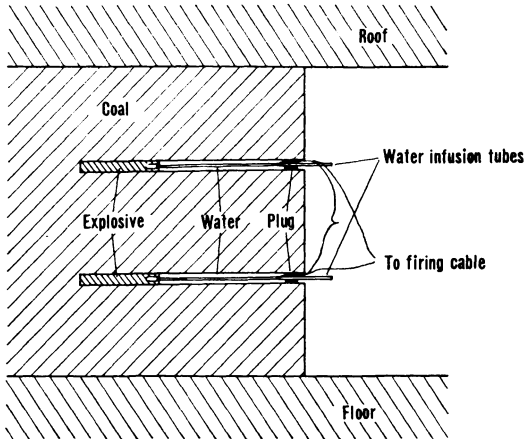
FIG. 14.6. Pulsed infusion round.

An even simpler means of avoiding undercutting is now being pursued, which introduces also the advantage of allowing short delay detonators to be employed. In solid coal there is no danger of breaks as in the situation considered above in ripping, but there is the possibility that the first explosive fired may cause the end of the boreholes of later shots to be broken, so exposing the explosive. A new class of explosive, known as P5, has been designed with the object of avoiding ignitions under these circumstances (see p. 87). This is particularly valuable in stable holes used in mechanical methods of mining. A wedge cut, or similar cut, as used in tunnelling is employed to produce a free face with zero delay detonators. Holes on each side are then fired with longer delay periods and the stable hole can then be cut with a single round of shotfiring. For reasons of safety, the longest delay period allowed is usually 100 or 200 ms so that there can be no time for appreciable release of methane from pockets of gas. Also the number of shots is, in practice, limited to twelve, as this is currently the capacity of the most powerful exploder which can be guaranteed to be safe for use in gassy mines.

The policy of the National Coal Board is to increase mechanisation in the mines for reasons both of safety and economy in personnel. This process has had considerable success on long wall faces and the majority of these are now worked mechanically. On a few faces complete remotely operated mining is possible at present. The process of mechanisation will

no doubt extend to other parts of the mine, but here the rewards are less and the convenience and simplicity of explosives ensure that they are likely to continue in use for many years.

Other Mines

In Britain mining is carried out, apart from coal mines, for anhydrite and gypsum, for iron ore, for non-ferrous ores and for salt. A common method used in this type of mining is known as pillar and stall working, illustrated in Fig. 14.7. The ore, or rock, which is usually in thick seams, is extracted over the whole area of the field, but leaving pillars which support the strata above and prevent the roof from falling in. The area occupied by
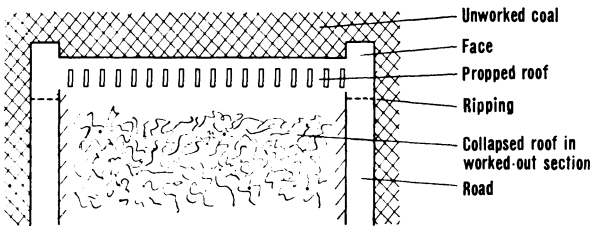
(a) Long-wall working
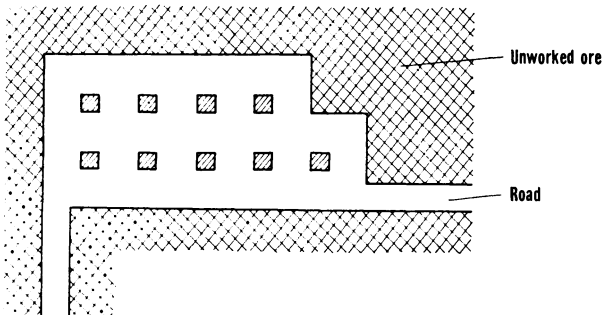
(b) Pillar and stall working

FIG. 14.7. Two methods of mining.

the pillars may be as much as a quarter of the whole area of the mine. When a particular mine is worked out it is possible to extract the pillars and allow the upper strata to subside.

The method of mining is somewhat like driving two sets of tunnels at right angles through the strata. Most mines of this type do not present any hazard from methane and therefore non-permitted explosives can be used. The selection of powder or gelatine type of explosive depends on the nature of the rock and particularly on the wetness of the mine.

As Britain is relatively poor in mineral deposits, this type of mining is less important here than in other countries of the world. The gold mines in South Africa, metal mines in the U.S.A., Canada and Sweden all use considerable amounts of explosive. In such mines the methods of working are often appreciably different from those described above and adapted to very large-scale production.

Quarrying

The process of quarrying is used to obtain road metal, rock for civil engineering purposes, limestone for steel making and is analogous to obtaining coal from opencast sites where the coal is at or near the surface of the ground. The methods used in quarrying can differ considerably in detail concerning the application of explosives, but the commonest is illustrated in Fig. 14.8. A quarry is worked as a series of benches, the
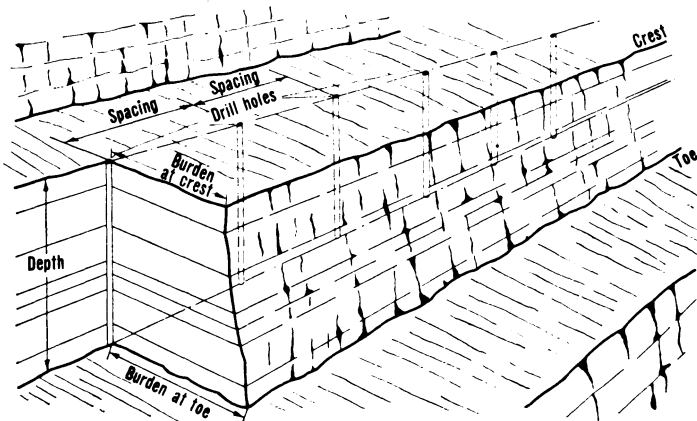
FIG. 14.8. Benching method of quarrying.

height of each being conveniently 15 or 18 m. The width of each bench is sufficient to allow access to loaders and lorries, so that each bench can be used as an entity.

To bring down the rock a series of holes is drilled from the surface down to the depth of the bench, or 0·3 to 0·6 m greater. If the bench is 18 m high, the holes can conveniently be 10 cm in diameter, 3·5 m back from the existing face and 3·5 m apart. They may be drilled either vertically, or at an angle of 70 to 80°. A row of such holes is fired at a time and the effect should be that the rock in front of them should slump into a heap of boulders of a size suitable for loading and crushing.

As the major expense in this operation is the drilling of the holes, it is usual to space them as far apart as possible and this is best achieved by the use of the strongest explosives. Under these conditions 9 tonnes of rock can usually be broken per kg of explosive. The amount of explosive to be charged in the drill holes is calculated from a ratio such as this. In the example quoted, each borehole will contain approximately 70 kg of explosive. If the conditions are at all wet, a gelatinous explosive is used, particularly at the foot of the hole. Under dry conditions, or in the upper part of the hole, where the work to be done by the explosive is less, weaker explosives can be used and ANFO is often suitable. The holes are charged, either by lowering cartridges downwards, or else by pouring in free-flowing explosive, such as ANFO.

The charges can be fired with electric detonators, but the commoner method is to use detonating fuse, usually known in Great Britain as Cordtex. This is capable of initiating gelatine explosives, such as Opencast Gelignite, without the extra use of a detonator. It is also a convenient method of connecting boreholes together. The method of application is shown in Fig. 14.9 A trunk line of Cordtex lies on the bench of the quarry and from this branch lines extend down the holes to the bottom. Frequently with large holes two lines of Cordtex are employed to make certain of initiation under all conditions, because in a large quarry blast a single failure from any cause can be extremely expensive. It is an advantage to arrange for the holes to be fired in succession by a series of short delays and this is done by inserting in the trunk line special delay connectors which give time lags of 15 ms. When the shot is fired, most of the noise comes not from the main charge of explosive itself, but from the Cordtex on the surface of the quarry. This noise can, however, be considerably reduced by covering the Cordtex with sand or stone dust.
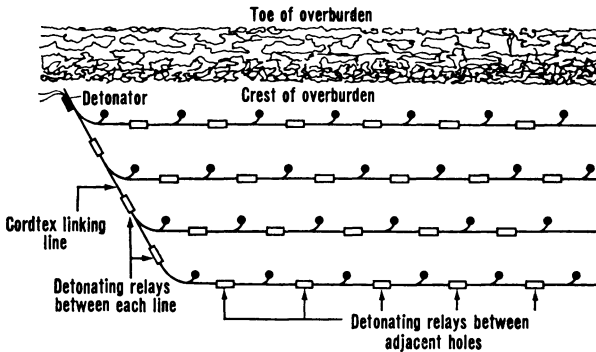
FIG. 14.9. Quarrying with Cordtex and detonating relays.

Removal of rock is required for many civil engineering purposes, and uses explosives in a manner similar to quarrying. An interesting technique is that known as pre-splitting. In this holes are drilled on the line of the proposed edge of the roadway, or cutting. These are filled with blasting explosives in relatively low charge, but the holes are drilled close together. When the explosive is fired a crack is formed along the line of the holes, but with little or no damage to surrounding rock. Subsequently the rock is removed by normal blasting and breaks away cleanly at the line of holes. This in suitable cases leads to a well-formed face of solid rock which can be finished by the minimum of concrete or other preparation.

No matter how well a blasting operation is carried out, there is liable to be some amount of rock left in the form of boulders too large to be handled by normal equipment. This is an inevitable result of lack of uniformity of rock. These boulders are broken down in size by a process known as secondary blasting. The usual method is to drill holes into the boulders, load them with explosives and fire. In certain cases the explosive can be placed on the surface of the boulder, covered liberally with clay or other material, and then fired. A cheap and effective way of detonating such charges is with safety fuse and detonators, the lengths of the fuse being arranged so that the shotfirer has ample time to get to safety. The Regulations do not allow more than six ends of safety fuse to be lit at one time by a shotfirer. Instead, the ends are connected to igniter cord (see p. 131). The shotfirer then has to light only the end of the igniter cord before retiring to a prepared position.

Seismic Prospecting

Sound waves in the ground are reflected at the boundaries between strata in the same way as sound waves are reflected from walls of buildings, etc. In seismic prospecting use is made of this by generating a wave with a charge of explosive and observing the reflections by means of geophones placed at suitable positions. This enables a geological map of the substrata to be drawn and indicates to the explorer the sites most likely to contain oil. This prospecting can be carried out either on land or at sea.
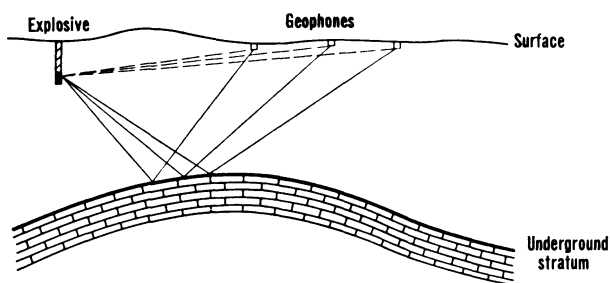
FIG. 14.10. Seismic prospecting by reflection method.

Figure 14.10 illustrates the method of seismic prospecting on land by what is known as reflection shooting. A hole usually 10 to 12 cm in diameter is drilled to a depth of 15 to 30 m. The charge of explosive is likely to be 5 to 12·5 kg and the stemming used is usually water. As the explosive must fire under a depth of water which may exceed 45 m, special varieties of gelatines are employed (see p. 53). Alternatively, a powder explosive can be sealed into pressure-resistant metal containers. Special detonators are also employed, not only to withstand the possible head of water, but also to have a specially short bursting time (see p. 113).

Seismic prospecting is also carried out at sea, the explosive charge being in a metal container and the geophones stretched along a cable from the stern of a ship. Either one or two boats may be used; charges are fired and records taken at regular intervals while the vessels are steaming. The explosive must be fired near the surface of the water, otherwise, as noted in Chapter 2, a bubble is formed which oscillates and passes into the water a series of shocks; the seismographic recordings then obtained are unsatisfactory for analysis. When the explosive is fired within 1·2 or 1·5 m

of the surface, the bubble is not formed, as the gases are immediately discharged into the atmosphere. In recent years prospecting for oil in the North Sea has been on a large scale and several thousand tonnes of explosive per annum have been used.

Miscellaneous Uses

There are many miscellaneous applications of explosives which may be mentioned but which do not merit individual description. Such uses are those in agriculture, in the preparation of ditches, the diversion of streams, removal of tree stumps, and the breaking up of subsoil. Demolition of old buildings and chimneys is readily carried out. Underwater wrecks may also be broken up for disposal by special application of explosive charges.

Of special interest is the civilian application of shaped charges developed initially for military purposes (see Chapter 15, p. 158). One such application is the blast furnace tapper illustrated in Fig. 14.11. In this

Plastic case   Metal cone   Explosive   Detonator
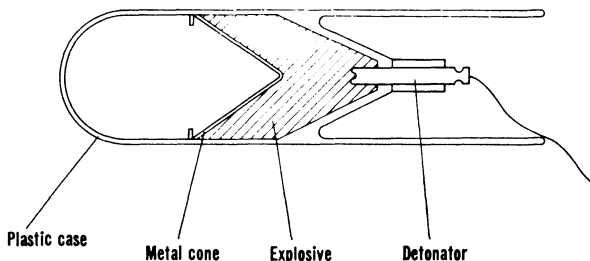
FIG. 14.11. Shaped charge for tapping blast furnaces.

the conical charge is used to penetrate a clay plug which seals the outlet of a blast furnace, and affords a quicker and safer method than the normal oxygen lance. Wedge-shaped charges have been developed for the cutting of submarine cables for lifting for repair.

In recent years much attention has been paid to the use of explosives for the shaping and working of metals. Figure 14.12 illustrates a simple application of the process for forming a dished end of a vessel. A flat metal blank is placed over a suitable mould and the space between them evacuated. Above the blank is water and in this a suitable explosive charge is fired. The metal takes the form of the mould with little or no spring-back and usually does not require further treatment. The process is particularly
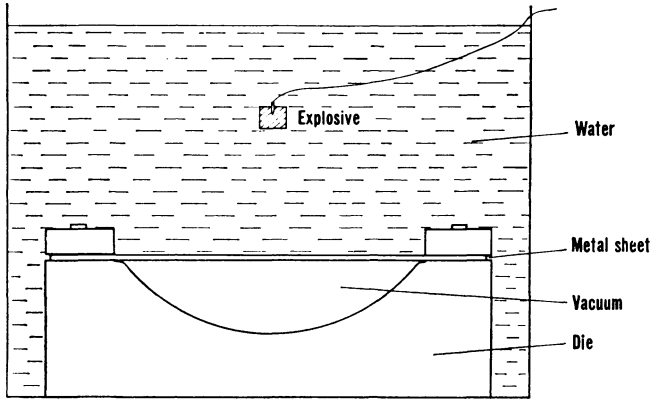
FIG. 14.12. Forming metal with explosive.

suited to the preparation of small numbers of complicated shapes, as no expensive equipment is required. It is therefore of particular interest in the production of prototypes for aircraft, missiles, etc.

An application of increasing importance is in the cladding of metals. In this a layer of explosive is used to project the cladding on to the base metal at such a speed that the two become firmly welded together. Fig. 14.13 shows one technique for small items where the cladding is at an angle to
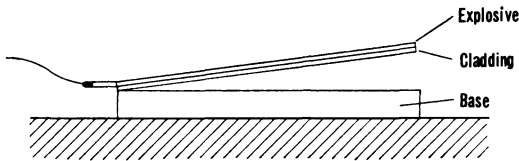
FIG. 14.13. Cladding metal with the use of explosive.

the base, which is firmly supported. The best results are however obtained by supporting the cladding parallel to the base plate and a short distance from it. The explosive used must have a suitable velocity of detonation, somewhat lower than the velocity of sound in the metals. The cladding and the base become welded with a wavy interface; the durability of the bond is such that the clad can readily be rolled or fabricated. Many combinations have been successfully made, of which the most note-worthy is probably titanium clad steel.

Many other applications of explosives could be described, but the ones

mentioned above are those of the greatest magnitude. Often those applications which use the smallest amounts of explosives are technically the most interesting, as they demonstrate best how accurately mechanical effects can be produced in minute fractions of a second.

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Military Applications

THE first offensive weapons used by man were probably stones, and similarly the first objects thrown when mortars were developed were solid, usually spherical, balls of stone or iron. With the development of explosives it was soon realised that it would be more effective to use a hollow missile filled with explosive, designed to burst in the middle of the enemy. Gunpowder was originally used as filling, but has now been completely superseded by high explosives.

It is convenient to differentiate between three broad classes of use of high explosive fillings.

  (a) The explosive is designed to rupture its container into fragments which are projected as shrapnel against enemy personnel.
  (b) The explosive is used to produce a blast effect against enemy buildings and equipment.
  (c) The explosive is used to penetrate targets such as armoured vehicles.

For the first purpose relatively small amounts of explosive are used and the nature of the explosive is of secondary importance. For the other purposes, however, larger proportions are necessary and for maximum effect the most powerful explosives are required.

Grenades

The modern equivalent of a stone thrown by hand is the hand grenade, of which the best-known form is the Mills bomb illustrated diagrammatically in Fig. 15.1. The steel shell is thinned along crossing lines, so that on explosion it is broken into fragments of predetermined size. When the grenade is thrown the lever is released and allows the

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striking pin to fire a percussion cap. This in turn lights a short length of safety fuse which takes 4 s to burn. At the end of this time the fuse fires the detonator which in turn initiates the main explosive charge. The normal modern filling for this type of device is an explosive based on TNT, filled as a powder. Other variants of hand grenades can use pressed charges of TNT or Amatol, or cast explosive. Instead of using the shell of the grenade to provide the shrapnel, it is possible also to use small metal objects, such as nuts and bolts, or coils of wire wound round the explosive charge.
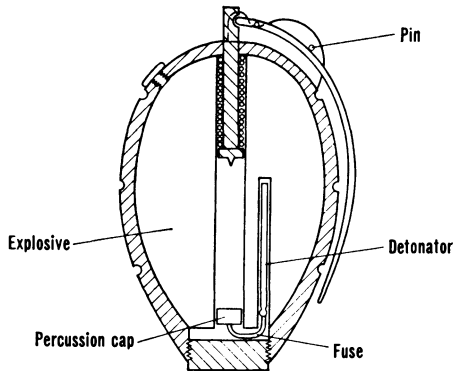
FIG. 15.1. Hand grenade.

Grenades can also be projected from rifles and then have a longer range. Their construction is, however, essentially the same.

Many other devices for use by hand have been invented. Mention may be made of limpet charges which usually employ magnets to make them adhere to the metal sides of tanks or ships. The explosive filling for such charges is a high velocity high power explosive such as cast RDX/TNT.

Shell

The first explosive bodies fired by mortars consisted of hollow spheres containing gunpowder which was ignited by a length of fuse, in turn ignited by the propellent gunpowder. The modern general purpose shell is illustrated in Fig. 15.2. It consists of a hollow steel shell with a cylindrical body and a head of ogive shape. Near the base of the shell is the driving

band, made of copper and which takes the form of the rifling of the gun during firing. The base of the shell is covered by a metal plate, the purpose of which is to prevent any hot gases from the propellant penetrating through joints or flaws in the body and igniting the high explosive charge prematurely. In a typical shell the fuze is contained in the nose and may be of several types according to the time at which the shell is required to explode.
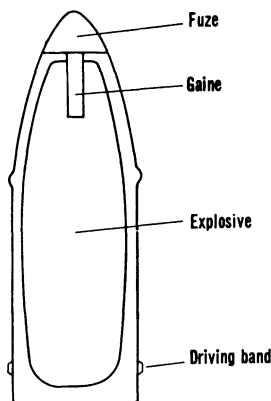
FIG. 15.2. High explosive shell

The shell has a dual function of producing fragments as an anti-personnel weapon and also producing blast against enemy installations. For the latter reason, the explosive charge should be of high density and power. Common fillings are therefore TNT, Amatol, or RDX/TNT mixtures, usually filled into the shell by casting. Because of the low density of the explosive compared with the metal, the actual weight percentage of explosive in the total shell is likely to be about 15 to 20%.

Shell for penetrating armour have heavier steel bodies with at least the nose of specially hardened metal. The proportion of explosive is smaller and it must also be exceptionally resistant to detonation by impact, so that the shell can penetrate the armour before the explosive is detonated by the fuze. Suitable fillings are therefore TNT or desensitised TNT/RDX mixtures. The latest armour-piercing projectiles for anti-tank use contain no explosive, but have high density cores made of tungsten.
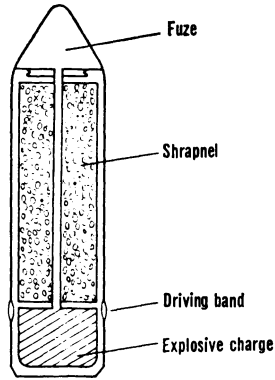
FIG. 15.3. Shrapnel shell.

The well-known shrapnel shell, used for anti-personnel purposes, is of quite different construction and is illustrated in Fig. 15.3. The base and sides of the shell are of heavy construction, but the nose is relatively weak and contains a fuze which is easily ejected by the explosive charge from the body of the shell. Immediately behind the fuze is a filling of metal shrapnel, often bonded relatively weakly with resin. The explosive charge is at the base of the shell behind the shrapnel. After a time of flight determined by the setting of the fuze, the explosive charge detonates and projects the shrapnel forward out of the shell as an expanding cone. In modern warfare the shrapnel shell is becoming of limited importance.

Bombs

Bombs carried by aircraft can be made of lighter construction than shell, because they do not have to resist the acceleration of firing from a gun. The general construction is shown in Fig. 15.4, but differences exist according to the detailed purpose for which the bomb is to be used.

Anti-personnel bombs have a relatively heavy casing containing an explosive such as Amatol, sufficiently strong to break the casing into fragments on impact. Bombs intended to produce a blast effect against buildings have a lighter casing and are usually filled with an explosive containing aluminium to increase the blast effect. Armour-piercing bombs
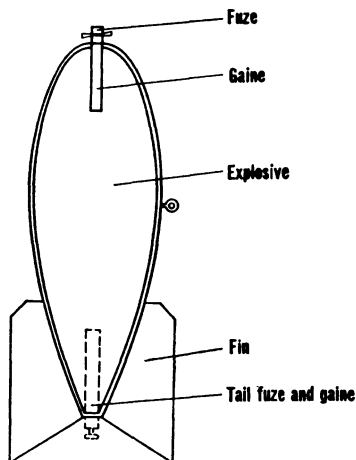
FIG. 15.4. Aircraft bomb.

for use against warships resemble armour-piercing shell in their type of construction and have heavy bodies with smaller high explosive charge. In the proper functioning of all these bombs, design of the fuze is of paramount importance.

Torpedoes

The explosive charge in a torpedo is carried in the nose, the rear compartments containing fuel and motor, together with the control equipment. As the torpedo must penetrate the ship to give the best effects, the nose is of heavy steel construction and the fuze operates with a delay. The high explosive charge must therefore be of maximum density and power. As the torpedo operates under water, the shock wave is considerable and advantage can well be taken of the increased energy given to explosives by the addition of aluminium. A common filling is therefore Torpex which consists of a mixture of RDX, TNT and aluminium and which has a high density, high power and high velocity of detonation. Maximum density is attained by filling the head of the torpedo by a carefully controlled casting process.

Depth charges for use against submarines are similar in principle to

bombs, but have their effect mainly by the shock wave produced under water. They therefore have relatively light shells containing a dense explosive of high velocity of detonation and high power. Cast RDX/TNT mixtures, with or without aluminium, are suitable for this purpose.

All the explosives used for military purposes are in general very insensitive and except in the smallest hand grenades a gaine or booster is used to ensure proper initiation. Such gaines are usually made by compressed pellets of tetryl inserted as a column into a metal tube inside the explosive charge.

Shaped Charges

Increased protection to military personnel, particularly in the development of armour-plated vehicles, has led to a rapid growth in importance of weapons using shaped charges of explosive. The effects of shaping the explosive itself were observed independently by Munroe and
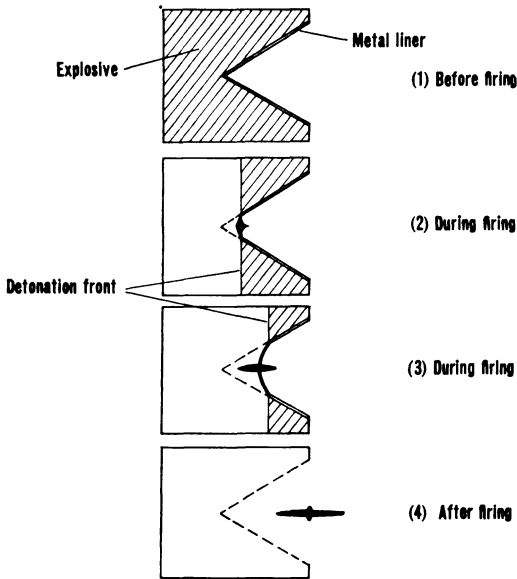
FIG. 15.5. Shaped charge-formation of jet and slug.

Neumann, but the development of practical charges with linings was due to a large number of workers.

If a conical depression is made in the end of a column of explosive, the shock wave is concentrated along the axis of the charge, which then has increased local penetration of metal or stone. A different and much more pronounced effect is achieved if the cone is lined with metal, as this forms a jet followed by a slug; the jet is projected forward at high velocity and can penetrate to great depths, giving a long, almost cylindrical hole. The stages of formation of the jet are illustrated in Fig. 15.5. In a sense, the cone is turned inside-out and collapsed, a process only complete some distance in front of the charge, so that a stand-off distance of one or more charge diameters is needed to ensure maximum penetration. A diagrammatic practical design of a shaped charge is shown in Fig. 14.11 (p. 150), where the explosive is shaped to give maximum economy, and the case provides an automatic stand-off.

The penetrating power of a shaped charge is approximately proportional to the cube of its diameter, but also very dependent on maintenance of exact axial symmetry during construction. It is also proportional to the detonation pressure of the explosive used, so that suitable fillings are cast Pentolite or RDX/TNT. Well-known applications of shaped charges are in the British PIAT and American bazooka.

A recent alternative to shaped charges is known as the squashhead projectile. As the name implies, this contains a plastic explosive which spreads on impact so as to make contact with the largest possible area of the tank before detonating. When the explosive detonates, reflection of the shock wave causes a scab of metal to be displaced from the inside surface of the armour plate (see p. 135). The effect inside the tank can therefore be greater than is the case with a shaped charge which may do little more than penetrate the armour. The amount of scabbing is approximately proportional to the area of contact of the explosive at the moment of detonation.

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Part IV.   Deflagrating and Propellent Explosives

Introduction

GUNPOWDER was first employed as a propellent explosive in guns, although later it was also employed for blasting. In neither case, however, does it detonate in the same way as the blasting explosives described in Part I, or the initiating explosives described in Part II of this book.

As a gun and rifle propellant, gunpowder had serious disadvantages. It was rather unpredictable in use, extremely dirty and caused considerable fouling of gun barrels. It also emitted an excessive amount of smoke and flash which immediately disclosed the position of the gun to the enemy. When Nobel and Abel invented ballistite and cordite respectively, many of these disadvantages were immediately overcome. Gelatinised nitrocellulose was soon found in France to have similar advantages. Gunpowder is no longer used as a propellent explosive.

Gunpowder was supplied in pellet form as a propellant and the substitutes were similarly manufactured. They were therefore called powders. Subsequent developments have led to the provision of propellent explosives in special and often massive form. Nevertheless, the term powder is still retained for their nomenclature, and the individual unit of the charge, no matter how large, is still called a grain.

Although these explosives do not detonate under conditions of practical use, this does not mean that they are incapable of detonation. The possibility cannot be ignored when large quantities are being handled.

Blackpowder

Manufacture

The raw materials potassium nitrate, charcoal and sulphur are first brought to a fine condition. Potassium nitrate must be ground by itself, but the charcoal and sulphur may be ground together or separately according to individual requirements. This grinding is frequently carried out in steel ball mills. The products are then sieved to remove any oversize or extraneous matter.

Appropriate quantities of the raw materials are added to a mill for intimate mixing and grinding. The mills used are of edge runner type in which a cast iron pan carries the blackpowder and the edge runners are large cylindrical wheels of steel, each weighing about 5·5 tonnes. These wheels are suspended with a clearance of about 6 mm from the bed to reduce hazard, as contact with the wheels is solely with blackpowder and friction between iron and steel is avoided. The charge of a blackpowder mill is about 125 kg. During mixing the wheels are rotated and roll on the blackpowder, whilst ploughs carry the material spread sideways by the wheels back into their path. Throughout the milling operation water is added to maintain a moisture content of 1 to 1·5%; this reduces the danger and also increases efficiency by assisting the incorporation of potassium nitrate into the charcoal. The milling process takes from one to seven hours according to the nature of the product required.

The mill cake taken from the mill is broken by passing between toothed gunmetal rolls to produce powder, which is then pressed between brass plates in a hydraulic press to a pressure of about 7 MPa, depending on the properties finally required. The purpose of the pressing is twofold. On the one hand it increases the intimacy of contact of the ingredients and improves the burning properties of the powder. On the other hand, it

increases the physical strength of the powder and reduces breakdown of the finished grain during transport and use.

The press cake is broken by passing it between gunmetal rolls, usually toothed. The coarse product thus produced is subjected to the corning operation. This consists of passing the material through a series of metal rolls which progressively break down the grain into smaller size, and sieving by shaker sieves. The required sieve size is extracted for further processing, coarse material returned for regrinding and fine material for reprocessing.

The sieved grains are glazed or polished by rotating in a drum for a period of about 6 h, frequently with the addition of a small amount of graphite to give a surface polish. This glazing process gives a rounded grain which is free flowing and which has increased resistance to moisture. The product is finally sieved to remove any dust.

To ensure adequacy of manufacture, blackpowder is subjected to a number of tests of which the following are probably the most important. The burning speed of the powder is determined, usually by making up a length of lead fuse and determining its burning speed. The rate of burning under confinement is measured in a "prover" which is a closed vessel with a piezo-electric pressure gauge and cathode ray oscillograph. The trace on the oscillograph gives the maximum pressure reached and also the rate of combustion to this stage.

Most blackpowders contain 75% of potassium nitrate, 15% of charcoal and 10% of sulphur. For safety fuse, however, blackpowders are made with reduced amounts of potassium nitrate. Also manufactured are sulphurless powders, containing approximately 70% of potassium nitrate with 30% of charcoal. These sulphurless powders are used for ignition purposes where sulphur could cause corrosion of metallic components.

Properties of Blackpowder

The density of blackpowder is usually about 1·7, but depends on the compression during the pressing process. There is a wide range of sizes, varying from about 12 mm diameter to material which passes a 150 mesh sieve. Blackpowder is ignited readily at a temperature of about 300°C for

the normal product, or 340°C for the sulphurless meal. It is hygroscopic at humidities exceeding 90% and then rapidly ceases to burn.

The properties of blackpowder depend considerably on the charcoal used. Soft woods freed from bark give the best results. Alderwood and dogwood are best, but the cheaper birch and beech are frequently used for ordinary purposes. In any case, it is important that the woods should be carbonised to the correct extent and this depends on the nature of the wood. In the case of alder, the optimum carbon content is 74%, whereas with birch a figure of 82% gives the best results. In general, if the carbon content is too low a readily ignited blackpowder is obtained but it has slow burning properties. It is also difficult to manufacture. If the carbon content is too high the material is easy to grind and milling is rapid, but the final blackpowder may be difficult to ignite and irregular in burning.

The burning speed of the powder in the lead fuse test can also be varied by changing the potassium nitrate content. The maximum burning speed is usually observed at a content of rather less than 70% of potassium nitrate.

It was shown by Vieille that the rate of burning, R, of blackpowder depends exponentially on the pressure, p, by the following equation:

$$R = ap^n$$

a and n being constants.

Mechanism of Combustion of Blackpowder

The mechanism of combustion of blackpowder is extremely complex and only an outline can be given here. It will be convenient to consider first the initial chemical reactions in ignition, then the reactions which occur during the main combustion and finally the nature of the products.

Hofmann and Blackwood and Bowden have studied the chemical changes which occur at temperatures approaching 300°C, which is the temperature of thermal ignition of blackpowder. That the process involves gases is shown by the proof by Blackwood and Bowden that ignition can occur at hot spots at temperatures as low as 130°C, provided that the local pressure is at least 150 atm. An important part in the reaction is played by a constituent of charcoal which can be extracted with acetone and shown to contain carbon, hydrogen and oxygen. Sulphur can react with this substance at temperatures as low as 150°C to produce hydrogen sulphide,

which in turn can react with potassium nitrate at about 280°C to give potassium sulphate. Also at about 280°C the organic constituent of charcoal can react with potassium nitrate with the liberation of nitrogen dioxide. The direct reaction of potassium nitrate and sulphur to give potassium sulphate and oxides of nitrogen commences at about 250°C, but becomes rapid only above the melting point of potassium nitrate, 330°C.

At temperatures below 300°C, the evolution of hydrogen sulphide is sufficient to reduce the nitrogen dioxide also produced, with the formation of sulphur and nitric oxide. As the temperature is raised, however, the evolution of nitrogen dioxide increases until there is excess which can react with sulphur to give sulphur dioxide and nitrogen. This sulphur dioxide can then react with potassium nitrate to give potassium sulphate in a strongly exothermic reaction. The heat produced in this reaction leads to further temperature rise and thus to mass ignition of the blackpowder.

The main process of combustion of blackpowder was studied exhaustively by Nobel and Abel and by Berthelot. These experimental results were examined in much greater detail by Debus, who has provided a self-consistent account of the chemical reactions involved. Debus considers that the overall reaction can be divided into two distinct stages: (a) a rapid oxidation process and (b) a slower reduction process.

The oxidation process is responsible for the actual explosion. Whilst it is no doubt complex, it can be simplified to the following overall equation:

$$10KNO_3 + 8C + 3S \rightarrow 2K_2CO_3 + 3K_2SO_4 + 6CO_2 + 5N_2$$

As the initial composition of blackpowder contains, for each 10 molecules of potassium nitrate, 14 molecules of carbon and 4 molecules of sulphur, this equation does not account for 6 molecules of carbon and 1 molecule of sulphur.

The excess carbon and sulphur take part in slower reduction reactions which are as follows:

$$4K_2CO_3 + 7S \rightarrow K_2SO_4 + 3K_2S_2 + 4CO_2$$
$$4K_2SO_4 + 7C \rightarrow 2K_2CO_3 + 2K_2S_2 + 5CO_2$$
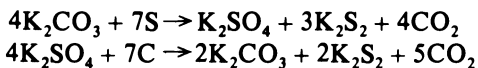
As the reduction is a slow process, it is not necessarily complete when the blackpowder has done its work. The reduction reactions are endothermic and lower the total heat evolution. On the other hand they increase the amount of gas evolved. Hofmann considers that these equations represent

only the overall reactions and that the actual paths are more complicated, involving the intermediate production of potassium monosulphide and of various gaseous products, including oxides of nitrogen.

As the reduction stage of the reaction does not necessarily go to completion the reaction products depend to some extent on the conditions of firing. In all cases, however, the chief products appear to be potassium carbonate, potassium sulphate, potassium disulphide, carbon dioxide, nitrogen and carbon monoxide, the last named arising either from the oxygen in the charcoal, or from side reactions. Side reactions give the by-products usually observed, namely, hydrogen, hydrogen sulphide, methane, ammonia, water and potassium thiocyanate. In most analyses small amounts of unburnt powder have also been observed.

Manufacture of Propellants

Introduction

Current propellent explosives may be divided into three classes: single base, double base and composite; however double base propellants which contain picrite are often considered a separate class and called triple base.

Single base propellants are basically nitrocellulose which has been made colloidal by the action of solvent.

Double base propellants contain nitroglycerine in addition to nitrocellulose and frequently other additives to give special properties. They can be manufactured by three methods and are then known as solvent type, solventless type and cast double base compositions. In the first method solvent is employed to ensure completeness of gelation of the nitrocellulose by the nitroglycerine. Such powders are used in small grain sizes. The solventless process gives a dimensionally more stable product as gelatinisation is performed without the aid of solvent. The method can therefore be employed for making larger grains for burning in small rockets and in gas-producing devices. Limitations of reasonable press capacity prevent even this method from being used for making the largest rocket charges. For this purpose the casting process is employed and the product is known as cast double base (CDB) composition. This process is generally employed only for the manufacture of rocket charges.

The third type of propellent explosive, the composite type, is a more recent development, the purpose of which is to provide rocket propellants of increased thrust, compared with the ordinary varieties. Composite propellants are based on an oxidising solid, commonly a perchlorate, together with an organic binder which both acts as fuel and gives adequate mechanical strength to the mixture. The search for even more energetic compositions continues, but because of the military importance of the

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results, little has been published. Table 17.1 from Kirk and Othmer gives typical compositions of single and double base propellants.

Single Base Propellants

As single base powders have been developed particularly in the U.S.A., their method of manufacture may be described as illustrating the principles involved. British practice is similar but often with omission of the "macaroni" pressing stage.

The nitrocellulose is first dehydrated, that is the water present is replaced by alcohol. This is done by compressing the wet nitrocellulose in a hydraulic press and passing alcohol through the press until the strength in the block is about 92%. The resulting block of alchohol wet nitrocellulose is broken down to small pieces with toothed rolls.

The incorporating process is carried out in mixing machines of the Werner Pfleiderer type, that is with two heavy horizontal blades in a specially shaped bowl. Incorporation consists of mixing the alcohol wet nitrocellulose and other ingredients with a solvent, normally ether and alcohol mixture. The amount of solvent used is adjusted so that the final consistency is that of a stiff dough.

This dough is transferred to a "blocking" press and there formed by the help of hydraulic pressure into solid blocks free from air. The blocks are then placed in a "macaroni" press, in which they are extruded through gauzes and dies into a mass of cords similar in appearance to macaroni. These cords are passed to a second block press so that a further block form is produced. These blocks are then placed in the final press, which has a die plate with dies of the correct size to give the physical dimensions required in the finished product. Above this plate is a series of gauzes to strain out any ungelatinised or foreign particles. The strands emerging from this press may be collected in a number of individual containers and then fed into a cutting machine. This cutting machine has rotating angled blades which brush the face of a perforated cutter bar. Strands are fed through the cutter bar by rollers geared to the rotating knives so that a constant length of cut grain is assured.

In an older cutting process still much used, strands are formed into a bunch which is then cut by guillotine.

TABLE 17.1   *Nominal Compositions of Smokeless Powders*

Constituent (%)	1	2	3	4	5
A. Partially colloided single base powders					
Nitrocellulose	80·00	89·00	87·00	84·00	
Barium nitrate	8·00	6·00	6·00	7·50	
Potassium nitrate	8·00	3·00	2·00	7·50	
Starch	2·75	1·00	—	—	
Paraffin oil	—	—	4·00	—	
Diphenylamine	0·75	1·00	1·00	1·00	
Dye (Aurine)	0·25	—	—	—	
B. Colloided single base powders					
Nitrocellulose	99·00	97·70	90·00	85·00	79·00
Dinitrotoluene	—	—	8·00	10·00	—
TNT	—	—	—	—	15·00
Di-n-butyl phthalate	—	—	2·00	5·00	—
Triacetin	—	—	—	—	5·00
Tin	—	0·75	—	—	—
Graphite	—	—	—	—	0·20[a]
Diphenylamine	1·00	0·80	1·00[a]	1·00[a]	1·00
Potassium sulphate	—	0·75	—	—	—
C. Double base powders[b]					
Nitrocellulose	77·45	52·15	51·50	56·50	
Nitroglycerine	19·50	43·00	43·00	28·00	
Diethyl phthalate	—	3·00	3·25	—	
Potassium sulphate	—	1·25	1·25	1·50[a]	
Potassium nitrate	0·75	—	—	—	
Barium nitrate	1·40	—	—	—	
Carbon black	—	—	0·20[a]	—	
Candelilla wax	—	—	0·08[a]	0·08[a]	
Methyl cellulose	—	—	0·10[a]	0·50[a]	
Dinitrotoluene	—	—	—	11·00	
Ethyl centralite	0·60	0·60	1·00	4·50	
Graphite	0·30	—	—	—	

[a] These constituents are added to the basic composition.
[b] Type 1 is the solvent type; types 2, 3 and 4 are the solventless type.

The cut powder is dried in stoves fitted with solvent recovery and operated to a carefully determined time schedule. If drying is carried out too quickly the surface can be hardened and afterwards crack, with serious effects on the ballistics of the resulting powder. This process of stoving

does not satisfactorily remove all the solvent and the last traces are removed by steeping in water at carefully controlled temperatures. The steeped powder is then dried by hot air.

Adequate ballistics cannot be achieved in single batches of propellants, even with closest control. It is therefore universal practice to take material from a number of batches of manufacture and blend them until correct and uniform ballistics can be ensured.

A common method of obtaining high rates of burning for shotguns, revolvers and pistols is the incorporation of potassium nitrate in the dough, followed by leaching of this potassium nitrate during the steeping process. In this way a product of controlled porosity and therefore controlled rate of burning is obtained. Such powders are also sometimes prepared in flake form by rolling into sheet and then cutting.

Rifle powders, particularly when porous, can burn so rapidly that the initial rise of pressure can be faster than necessary. In this case, the grains can be surface moderated, or given a surface coating of a nitrocellulose gelatiniser, such as dinitrotoluene, dibutylphthalate, or carbamate. This process is often carried out at the same time as glazing, with a small amount of graphite, which improves the flow properties of the powder as well as increasing its loading density.

Double Base Powders—Paste Mixing

In modern practice the use of dry guncotton is avoided for reasons of safety and the first stage in the process of manufacture, whether for solvent type or solventless products, is the formation of a paste from wet guncotton. The British methods by which this is done are described by Wheeler, Whittaker and Pike. There are in fact two methods which have been used. In one a slurry of finely pulped guncotton is made in water and circulated through a ring main. The concentration of the slurry is determined and then a suitable volume is measured in a tank. This is then passed, either with the original process water, or with previously used water, into a tun dish in which the slurry is sprayed with nitroglycerine. The slurry then passes to a mixing tank in which a stabiliser and chalk are added and the whole is stirred for a period of not less than 30 min.

Alternatively, the guncotton can be obtained in a water-wet condition in

which it contains approximately 30% of water. The water content is determined and the appropriate amount of wet guncotton for a batch is weighed out. This is slurried in water in a pre-mix tank and then nitroglycerine is run in with stirring. The product is transferred to a final mixing tank where it is processed as above.

The mixture is then run on to a sheeting table which is made on the same principle as a paper-making machine, but with the wire replaced for safety by a suitable cloth filter. The pulp passes over suction tubes and between rollers in order to remove as much water as possible, so that the paste when stripped from the cloth contains 20–25% of water. It is dried on trays or else in trucks through which air at 50°C is blown.

Solvent Type Double Base Propellants

Dried paste is weighed into incorporators, usually of the Werner Pfleiderer type. To the incorporators are added the appropriate amounts of other ingredients and also solvent which is usually acetone or a mixture of acetone and water. When mixing is finished a stiff dough is obtained. This is rammed into the cylinder of a hydraulic press at one end of which is a die containing holes of diameter depending on the cord size required. For cannon powders, for example, cord diameters are large and only a few are extruded. The cut cords are taken to a solvent recovery stove, where the acetone is removed and recovered; the final stoving to remove the last traces of acetone is sometimes given at a higher temperature. The powder is blended with extreme care so as to give completely regular performance.

Ball Powder

In the ball powder process, developed by the Western Cartridge Company, nitrocellulose is agitated with ethyl acetate solvent in aqueous suspension with emulsifying ingredients. This gives a suspension of spheres, the size of which can be controlled by the speed of stirring. The suspension is heated to distil off the solvent and harden the spheres, which after cooling can be impregnated with nitroglycerine and dried. If necessary the spheres can be rolled to decrease the web thickness and time of burning and they can be graphited according to requirements. The

process is particularly applicable to the manufacture of rifle powders, but it is also used in producing grains suitable for the slurry casting process.

Solventless Double Base Propellants

The use of solvent limits the size of grain which can be produced because of the difficulty of removing final traces of solvent and thus ensuring ballistic stability during storage. The solventless process overcomes this difficulty by attaining gelatinisation of the paste by the effect of heat and work. The dried paste is first passed repeatedly through hot rolls to a definite schedule of passes and roll settings. Reworked material can be blended in at this stage.

The sheets thus produced are cut into discs, or else formed into carpet rolls. The former process involves cutting circular or square portions from the sheets so as to fit the extruding press. These are examined for flaws and then compressed to form a "cheese". The latter process involves cutting the sheet into strips which are then rolled into "carpet rolls" of a diameter suitable to fit the cylinder of the extruding press.

The propellant is extruded hydraulically at pressures of 15–35 MPa. The press cylinders are heated and filled with heated discs or carpet rolls. In most modern practice the cylinders can be evacuated to avoid air bubbles in the final propellant. For the larger sizes, the press dies give a single large cord which is cut to length by a guillotine while still hot. After cooling it can be handled in wood-working machinery under suitable conditions to give exact length and for such purposes as slotting or drilling. For smaller sizes of grain, the process is similar to that for the solvent type product, but without the necessity of the solvent recovery stage.

Cast Double Base Propellants

Although the solventless cordite process enables grains of larger diameter to be made than are possible by the solvent process, it is nevertheless restricted to about 10 cm in diameter, owing to difficulties in maintaining dimensional stability and to difficulties in construction of adequate extrusion presses. The problem of producing larger grains of this type of propellant has been overcome by the introduction of the casting

process. This utilises a powder consisting of nitrocellulose and nitroglycerine, with any necessary modifiers, and a casting liquid which consists of nitroglycerine with suitable desensitisers. A case is filled with these ingredients to give an air-free heterogeneous mixture. It is then subjected to prolonged heating, so that the nitroglycerine swells the nitrocellulose until finally a homogeneous structure results.

In the simpler version of this method, a double based powder of small size is made by conventional solvent methods and thoroughly dried. The required amount of this powder is then placed in a "beaker" of cellulose acetate or ethyl cellulose and the voids are all filled with desensitised nitroglycerine. The curing process consists of heating to temperatures of the order of 80°C for a prolonged period and on cooling, the mass becomes a gelatinous body similar to cordite or ballistite.

In another version of this process developed in America, the grain and the nitroglycerine are formed into a slurry which is poured as such into the casing before curing. This process has been described by Boynton and Schowengerdt. The nitrocellulose is used in the form of a ball powder in granules which may vary from a few microns to a coarse mesh size. The nitroglycerine and other liquid ingredients are then placed in a simple mixing pot and the solid ingredients, including the nitrocellulose, added. After stirring for a few minutes the slurry is poured into a case and cured by heat.

It is possible in both the above processes to add oxidisers such as ammonium perchlorate so as to give propellants which combine the properties of the composite propellants and the more conventional double base type. It is claimed that the product can have an ultimate tensile strength of 800 kPa with an elongation of roughly 30%. These properties must, however, be sacrificed to some extent if the highest propellent performance is required.

Composite Propellants

Composite propellants consist of an oxidiser together with a plastic which serves the dual purpose of a binder and a fuel. Other ingredients, such as aluminium, may be added to increase the heat of combustion. The commonest oxidiser is ammonium perchlorate and the method of

manufacture will be described on this basis. Fuels of many types are used, mainly polymeric and usually of a rubbery consistency. Grains are made by casting, moulding or extrusion.

The first process in all cases is the production of the oxidiser in a suitable fine crystal size. A bimodal particle size distribution, obtained by mixing very fine with slightly coarser particles, often gives the best product. The fuel/binder is frequently prepared as a prepolymer so as to assist mixing and also to reduce the time of the later curing process.

In casting grains, the oxidiser and the prepolymer are mixed in equipment similar to the Werner Pfleiderer mixer. The resulting thick dough is subjected to vacuum to remove air bubbles, and cast either into moulds or directly into motors. With thermoplastic binders the mixing and casting are carried out hot and the charge is then allowed to cool by a carefully controlled process. With thermosetting binders the mixing and casting are carried out cold, but the charge is then cured at an elevated temperature for a time which may be one or more days. It is frequently necessary with charges of this sort for them to be bonded to the case and this is done by applying a case bonding to the case before casting. Careful control of all temperature changes is necessary to avoid shrinkage and to allow stress relaxation, otherwise the charge is likely to become separated from the case and may even crack. A continuous process for mixing and casting composite propellants has been described.

Polymers which give mouldable propellants are mixed with the oxidiser in a similar manner, but the product is usually worked mechanically between rolls and evacuated to remove air bubbles. The powder is then moulded by pressure into the metal casing. Alternatively, such plastics can give a propellant which can be extruded into charges which are afterwards cut and machined to suitable shape. The Rocket Propulsion Establishment at Westcott has used ammonium perchlorate and polyisobutene to produce a propellant of putty-like consistency.

In Britain grains of composite propellant containing 4000 kg have been fired. In the U.S.A. even larger charges are recorded, including a 3 m casing containing 100 000 kg of propellant.

Factory Construction and Operation

The main risk in the manufacture of propellants is that of fire and only in isolated circumstances is there also a detonation risk. A common construction of a building is therefore of reinforced concrete, and frequently one single building contains a number of compartments separated by strong partition walls. Each compartment will, however, have a blow-out panel of large size and flimsy construction. Should a fire occur the panel blows out and prevents any build up of pressure which could cause the deflagration to become more severe.

In certain operations, such as the rolling of solventless cordite, experience shows that fires must sometimes be expected. Under these circumstances it is usual to provide a water drenching system operated by a photoelectric device. Rapid application of a mass of water successfully limits the fire to the material originally enflamed.

It is an unfortunate characteristic of propellants that they invariably burn to detonation if there is more than a critical depth of powder above the point of ignition. This depth depends greatly on the composition and on the grain size. It may vary from about 10 cm to several metres. In processing, the critical depth for the product being made is not exceeded unless full precautions for handling a detonating explosive are taken.

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Properties of Propellants

PROPELLANTS, like all explosives, are intended to do work in a finite time. It is, therefore, with energy and burning speed that this chapter is mainly concerned. The method of approach differs from that with high explosives, because the hydrodynamic theory, so useful in that case, is of little value with propellants. If we refer to Fig. 2.4 of Chapter 2, it was shown that burning consists of a transfer from the initial point A to the lower portion EC of the Rankine–Hugoniot curve. In view of the relative slowness of the process, the pressure of the propellant and the products can be considered equal, so that the transfer is effectively along the line AE. Propellants, however, are always used in closed systems and the initial pressure (and final pressure) is no longer equal to atmospheric. Because the point A is defined only by the application of the propellant, the hydrodynamic theory gives no direct information. It does, however, tell us that the products of combustion stream backwards relative to the burning front and not forwards as in the case of a detonation wave.

The heat given out in the combustion of propellants is readily measured by exploding them in special calorimetric bombs built to withstand the high pressures produced. The result thus obtained, however, does not necessarily give exactly the heat available under practical circumstances, as in the calorimetric bomb the products are cooled and can undergo reactions which have different equilibria at high and low temperatures. It is, therefore, usual for design purposes to obtain the calorimetric value of a propellant also by calculation.

The calculation of the heat liberated in the burning of the propellant can be carried out in a manner similar to that described for high explosives. The pressures encountered are, however, much lower and correspondingly the gas densities also are lower. Simple equations of state are therefore

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adequate, and indeed for rocket propellants the combustion products are usually considered to behave as ideal gases. For gun propellants where the pressures are higher, the Abel equation of state is usually employed:

$$p(v-a) = RT$$

where a is a constant.

By constructing the Rankine–Hugoniot curve in the lower pressure region in this way, the volume, temperature and composition of the combustion gases can be calculated for various given operating pressures. In general the calculations must be carried out by successive approximation, but in the particular cases of single and double base compositions, simpler methods have been derived.

Calorimetric values of single base powders lie in the range 4000–3000 J g⁻¹ and for double base 5200–3000 J g⁻¹ for ammunition or down to 1750 J g⁻¹ for use in power cartridges.

The other particularly important property of propellent explosives is their rate of burning. This cannot be calculated but must be measured. The measurements can be carried out in a number of ways, but the simplest is by the strand burner particularly used for rocket compositions. This is illustrated in Fig. 18.1. A strand of the propellent composition, commonly 3 mm diameter and 15 to 18 cm long, is coated by a plastic so that it can burn only from one end. This strand is held inside a bomb pressurised with nitrogen and allowed to burn. The rate of burning is measured by timing the interval between the melting of fuse wires resting on the strand. Tests are carried out at a number of pressures and the variation of burning rate with pressure is thus determined.

It is found that the rate of burning increases approximately linearly with the calorimetric value and lies in the range 0·4–1·3 cm s⁻¹ at 7 MPa, although higher rates can be achieved.

This technique is much less suited to measuring the burning rates of propellants for use in rifles and guns. In these cases, it is not usually necessary to determine this rate accurately, but instead a measurement is made of the pressure developed in the actual use of the propellant. This is done by connecting a piezo-electric gauge to the chamber of a gun and recording the pressure change, during firing, by an oscilloscope.

The results of measurements made in these ways show that the rate of burning of a propellant depends markedly on the pressure. At the high
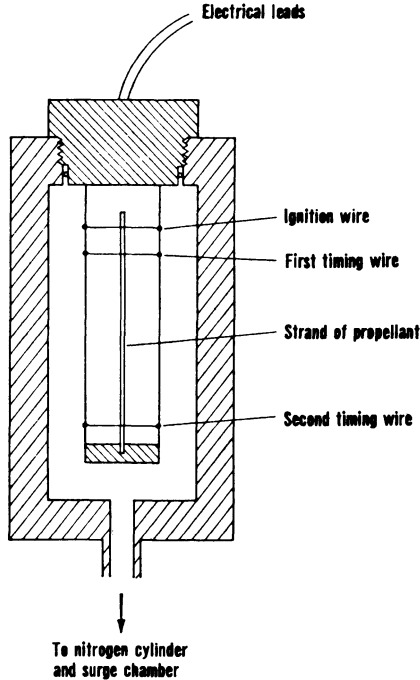
FIG. 18.1. Strand burner.

pressures used in guns (perhaps 300 MPa) it is often sufficient to assume that the rate of burning, R, is directly proportional to the pressure, p. Rather more accurate results can be obtained by using a formula of the following type:

$$R = b + ap$$

where b and a are constants.

At lower pressures, such as are encountered in rockets and power cartridges, the relationship preferred is the exponential form:

$$R = ap^n$$

This is known as Vieille's Law. The exponent, n, is known as the pressure index of the propellant and is usually in the range 0·5 to 0·8.

Vieille's Law is obeyed well by the older types of single and double base

propellants. Many of the more modern compositions do not obey this law. This is particularly true of low pressure propellants containing a platonising agent, the purpose of which is to make the burning rate practically independent of pressure over a useful working region. Nevertheless, it is convenient to use the Vieille equation even if it can be regarded only as an approximation and used only over a limited range of pressure.

The rate of burning of a propellant is also influenced by the initial temperature of the charge. The effect is much less than the normal effect on chemical reactions, but can still be important when the material is to be used over a wide range of temperatures from arctic to tropical and those encountered in supersonic flight.

A characteristic of propellent burning is that it proceeds by layers with the burning front always parallel to the surface. This is known as Piobert's Law, and it is on this law that the design of propellent grains depends. If, for example, we consider a long solid cylinder of propellant, then as burning proceeds the cylinder remains of the same shape but with gradually reducing radius. It is clear that the surface area of the propellant gradually decreases so that the mass rate of burning of the propellant also decreases. This is obviously undesirable and many means of avoiding it have been designed.

One common method of designing propellent grains is to use a long annulus. This can burn on both the interior and exterior surfaces, so that as burning proceeds the outer surface decreases, but the inner suface increases in such a way that the total surface and therefore mass burning speed remains constant. Similar properties are also shown by thin flakes or discs of propellant which are suitable for use for small arms ammunition.

For some purposes, it is indeed desirable that the rate of burning should increase during the process rather than remain constant. This is true in certain guns. For such purposes grains can be produced perforated by a number of holes so that the burning surface increases as combustion proceeds. For rockets special constructions are used which are discussed in Chapter 19.

Whilst the shape of a propellent grain determines the constancy or otherwise of the burning process, the actual time occupied depends on the grain dimensions. The term "web thickness" is used to denote the shortest distance in a grain through which burning can go to completion; it is

measured normal to the burning surface. The number of burning surfaces is ignored. Thus in small arms propellants it is customary to denote by web thickness the diameter of a cylinder or the thickness of a flake, even though burning is from both sides. On the other hand, rocket charges burn from one surface only, but the total thickness is still called the web thickness.

The actual process of burning of single and double base propellants has been studied in some detail and shown to consist of a number of stages, as shown in Fig. 18.2. The succession of stages is as follows.
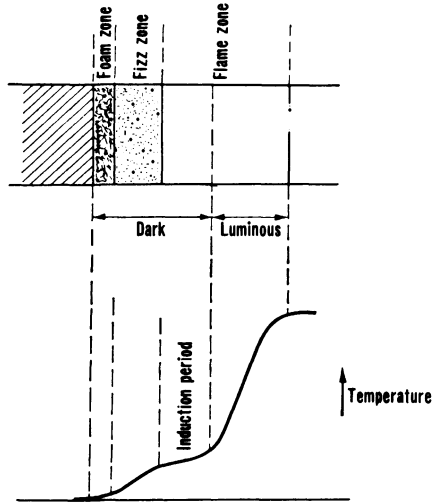
FIG. 18.2. Process of propellent burning.

Solid propellant is first caused by radiation and convection to melt and evolve sufficient gas to give a foamy structure. This is known as the foam zone. The gaseous products from this zone pass through the fizz zone where an initial reaction occurs. These intermediate products enter the flame zone where after a brief induction period they undergo the final reaction to the combustion products. It is only in this final reaction that there is any luminosity, so that the fizz zone and the initial stages of the flame zone are in fact dark. The actual thickness of this dark zone depends on the pressure under which the propellant is burning. Below 1·4 MPa the flame zone does not exist. When the pressure increases the dark zone decreases in thickness until at 7 MPa it can no longer be observed. These changes explain well the marked dependence of burning rate on pressure.

The burning mechanism of composite propellants differs from that described above. There is no exothermic reaction which can lead to a self-sustaining fizz zone. Instead, the first process appears to be the softening and breakdown of the organic binder/fuel which surrounds the ammonium perchlorate particles. Particles of propellant become detached and enter the flame. The binder is pyrolysed and the ammonium perchlorate broken down, initially to ammonia and perchloric acid. The main chemical reaction is thus in the gas phase, between the initial dissociation products.

The stability of propellants from both the chemical and physical points of view is of considerable importance, because they frequently have to be stored for many years under adverse conditions of temperature. Minor changes, such as could well be tolerated with high explosives, cannot be allowed with propellants because they would seriously affect the performance of the gun or other weapon. Accelerated storage tests, usually involving cycling between the extremes of temperatures likely to be encountered, are used to determine the long term stability of products. In the case of large grains, such as those used in rockets, physical strength and stability can be of great importance. Thus, it is usual to determine tensile strength and elongation under both static and dynamic conditions. Even more important is the examination of the grain for tendency to crack under conditions of varied temperature.

Many methods have been proposed and are used to study the thermal stability of propellants and to ensure the absence of possible autocatalysed decompositions during storage. None are sufficiently reliable to merit individual description. In practice, stabilisers are added, the usual being diphenylamine for nitrocellulose powders and symmetrical diethyl diphenyl urea (carbamate or centralite) for double base propellants. Provided a reasonable proportion of stabiliser remains, the propellant can be assumed to be free from the possibility of autocatalytic decomposition. The best test of stability is therefore a chemical determination of the stabiliser present.

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Design and Application of Propellants

A S PROPELLENT explosives comprise a wide range of products, each designed for a specific application, it is convenient to discuss their detailed design and applications at the same time. It is proposed to proceed in the order roughly of the smallest grains to the largest. In this way progression will be the more natural, even though a considerable degree of overlap must still remain between the individual classes.

Small Arms Ammunition

Small arms may be taken to mean weapons with a bore of less than 2·5 cm, whether the barrel is smooth or rifled. Compared with larger weapons, they have light bullets or shot and have relatively short barrels. Propellants used must therefore be fast burning and have small web thickness. The factors which determine design of powder depend also on the individual characteristics of the weapons.

In the case of shotguns, for example, experience shows that it is best to use shot weighing about 30 to 35 g in a weapon weighing between 3 and 4·5 kg. Heavier loads of shot, or lighter guns, give unpleasant recoil, whereas heavier guns become too unwieldy. Even at this weight of weapon, the barrel must be relatively thin, particularly at the muzzle where extra weight would lead to slowness in aiming. The working pressure which the chamber will stand is therefore relatively low and not likely to exceed 45 MPa. A powder which will burn fast at low pressures is required in small web thickness. The structure of a typical shotgun cartridge is shown in Fig. 19.1.

Pistols and revolvers have very short barrels and therefore the time during which the propellant must burn is very limited. Burning pressures can, however, be higher and are often in the range 75–110 MPa.
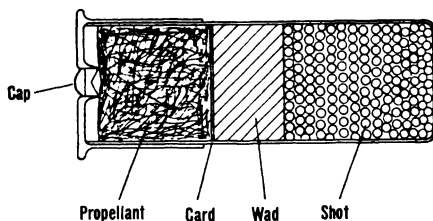
Fig. 19.1. Shotgun cartridge.

Compared with shotguns the higher pressure and shorter barrel length tend to cancel each other out and somewhat similar powders may be used.

The smallest common rifle is of 0·22 in (0·56 cm) calibre as used for target shooting. The weapons themselves have barrels which are neither particularly short, nor with any noteworthy restrictions on strength. On the other hand, the ammunition is of a particular type known as rimfire, as illustrated in Fig. 19.2. The name comes from the method of firing which is
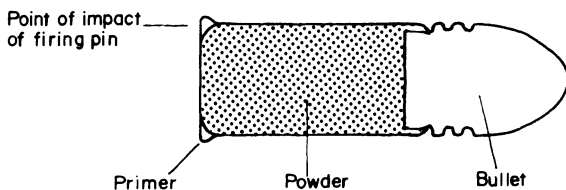
Fig. 19.2. Rimfire cartridge.

by the use of an eccentric striker which crushes pyrotechnic composition contained in the base of the cartridge between the walls and the rim. Such cases are soft and relatively weak and cannot withstand high pressures. The bullets also are of a relatively soft nature. It is these factors which limit the pressure at which the powder must burn to about 110 MPa. The small size of the cartridge also means that the grain must be small.

The larger rifles such as the familiar military rifle use cartridges of the type shown in Fig. 19.3. The relatively heavy base contains centrally a pyrotechnic percussion igniter (cap) and also a rim on which the ejector mechanism operates. Bullets can be made of various materials, but the detailed construction depends on whether they are to be used for armour piercing, anti-personnel, incendiary or tracer purposes. In operation, the primer is fired by the striking pin of the rifle, the propellant ignites and the

gas pressure causes the case to expand and form a gas-tight seal in the breech of the rifle. The bullet is projected forward, engages in the rifling where it forms a seal and also is driven forward in a spiral fashion. A working pressure of 300 MPa is common and burning times are longer than in the other weapons mentioned, so that web thicknesses can be somewhat higher. A major difficulty in design of these cartridges is to ensure that tracer rounds, in spite of the different weight and shape of the bullet, follow the same trajectory as the ball rounds.
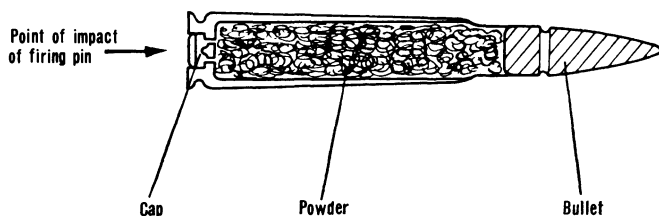
FIG. 19.3. Rifle cartridge.

For all these weapons there is a choice between single base and solvent type double base compositions. Much has been said on the relative advantages of these two types of powder. Double base powders are less susceptible to the effects of moisture and varying humidity, but they cannot successfully be surface moderated. Modern practice is to use these powders in such cases as shotgun shells where complete protection against humidity changes is difficult. Double base powders are used in smaller powder charge weights than single base and this largely offsets their tendency to give increased barrel erosion, due to the higher temperature of the combustion products. For the smallest grains, as for shotgun and rimfire cartridges, the usual form is a thin disc. The powder is made porous in order to give sufficiently rapid combustion. For the larger sizes, as in rifle cartridges, the larger web thickness makes possible the use of a tubular powder which has the advantage of improved loading characteristics. Details of some typical small arms propellants are given in Table 19.1.

Ordnance Propellants

The general design of a large round is similar in principle to that of a rifle cartridge, but the shell has the special construction described on p. 154.

TABLE 19.1   *Typical Small Arms Propellants*

Ammunition	Powder			
	Type	Shape	Dimensions	Web thickness
Shotgun	Double base	Porous disc	1·27 mm diam.	0·15 mm
Rimfire	Double base or single base	Porous disc	0·89 mm diam.	0·10 mm
Revolver	Double base	Porous disc	1·02 mm diam.	0·13 mm
Rifle	Single base	Tubular	1·27 mm diam. 0·38 mm diam.	0·46 mm

For weapons of larger size, the design of propellent charge can become a complicated matter of interior ballistics. Because of the long burning time, however, web thicknesses are large and multi-perforated grains can be produced to give suitable pressure–time curves.

A choice has again to be made between single and double base propellants. In the past double base propellants tended to be unpopular, because their original high calorimetric value caused gun erosion. This has now been overcome. Also the presence of nitroglycerine can give physiological effects under bad conditions; these, however, no longer occur in modern equipment. The main advantage of double base propellants is that they can be produced with low quantities of volatile material and also with high stability, so that their ballistic change during storage is very small. On the other hand, single base propellants have some advantages in manufacture and in general can be blended more readily to give required ballistics. Because of the wide variety of weapons, it is not possible to quote typical grain sizes of web thicknesses.

Ordnance propellants are required to give the minimum of muzzle flash, smoke and barrel erosion. All these objectives are assisted by adding to the propellant a proportion of nitroguanidine (picrite), made by treating guanidine nitrate with sulphuric acid and brought to very fine particle size by recrystallisation and disintegration.

For the largest weapons, the propellent charge can be kept separate from the rest of the round and in this way it is possible to adjust the weight of the propellant to allow for wear of the gun during continued use. The storage and handling convenience of a complete sealed round are, however, such that this is the form usually adopted.

Rockets

The design of propellants for solid fuel rockets differs considerably from that for ordnance, because of the lower operating pressures, usually below 15 MPa. To understand the principles involved it is first necessary to give a brief account of rocket propulsion. In this account considerations will be restricted to motors based on solid propellants. Motors based on liquid fuels, such as petroleum fractions and liquid oxygen, depend on combustion processes of non-explosive type.

A sketch of a rocket motor is shown in Fig. 19.4. It consists of a chamber, containing the propellant and an igniter, at one end of which is the nozzle. The nozzle has a restricted portion, or throat, which controls the rate of flow of the gas and a divergent portion which causes the exhaust gas to attain a high and supersonic velocity. The thrust on the rocket consists of two parts, the first due to the backward momentum of the gases and the second due to the difference in static pressure of the exhaust gases at the nozzle exit and the surrounding atmosphere. The latter component is usually designed to be small and is therefore neglected in the following discussion.
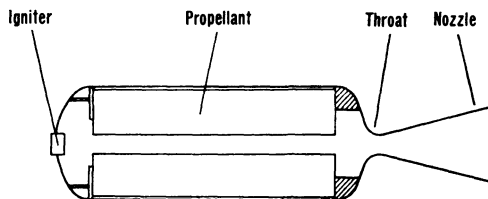
FIG. 19.4 Solid fuel rocket motor.

As there is no appreciable loss of heat from the rocket to the surrounding atmosphere, the internal energy of the propellant which is released on combustion appears in the exhaust gases, partly as kinetic energy, and partly as internal energy of the reaction products. If the internal energy of the original propellant is H_o and the internal energy of the exhaust gases H_e, then the kinetic energy is by difference $H_o - H_e$. If V is the velocity of the exhaust gases and M their mean molecular weight, it follows that

$$H_o - H_e = \tfrac{1}{2}MV^2$$

therefore $\qquad V = \sqrt{[2(H_o - H_e)/M]}$

For comparative purposes it is usual to consider the effect when unit weight m of the propellant burns in unit time t. As momentum is equal to impulse in a flow system, then $Ft = mV$ or, as t and m are both equal to 1, $F = V$. Thus for the propellant the specific impulse I_{sp} is given by

$$I_{sp} = F = \sqrt{[2(H_o - H_e)/M]}$$

H_o can be calculated from the propellant composition, but H_e must be obtained by successive approximation, assuming that the final state of the exhaust gases is known. For present purposes, it is sufficient to note that $H_o - H_e$ correlates well with the heat of explosion of the solid explosive. In order to obtain the maximum thrust from a rocket it is therefore necessary to achieve the highest combustion temperature, but also necessary to produce gases with the lowest mean molecular weight.

The composition and properties of an American solventless double base composition have been published and are quoted in Table 19.2. This powder is known as JPN and is processed by solventless extrusion.

TABLE 19.2 *Rocket Propellant JPN*

Composition	%
Nitrocellulose	51·5
Nitroglycerine	43·0
Diethylphthalate	3·25
Carbamate	1·0
Potassium sulphate	1·25

Carbon black (0·2%) and candelilla wax are also added.

Properties	
Burning rate (7 MPa)	16·5 mm s^{-1}
Pressure index	0·7
Molecular weight of products	26·4
Specific impulse	250 s

According to Sutton, cast double base charges are likely to contain 45–55% nitrocellulose, 25–40% nitroglycerine, 12–22% plasticiser and 1–2% other ingredients such as stabilisers. Typical properties are:

Burning rate (7 MPa)	5·6–9·4 mm s^{-1}
Pressure index	0·1–0·8
Molecular weight of products	22–28
Specific impulse	160–220 s

For composite propellants the properties depend on the proportion of binder, and also on whether high energy fuels such as aluminium have been added. Figure 19.5, taken from Barrère, Jaumotte, de Veubeke and Vandenkerckhove, shows how the specific impulse depends on these factors.
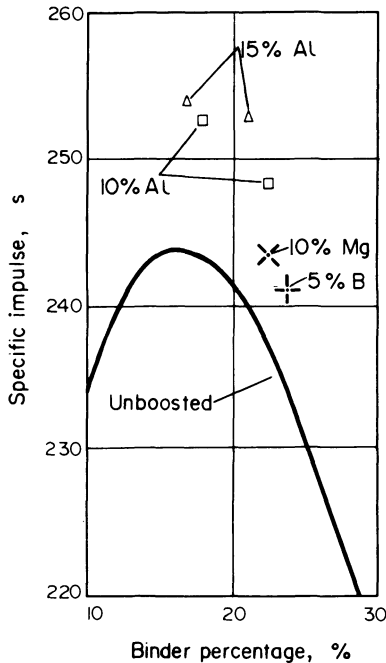
FIG. 19.5. Specific impulse of composite propellants.

The design of the grain is as important as the selection of the propellant. A rocket is required to have a uniform thrust throughout the period of burning. As the grains, like all propellants, obey Piobert's Law, it is necessary to achieve a uniform area of burning surface through the whole process of burning. As the motors are in general cylindrical, the propellent grain must follow this shape in external diameters. In the most important

case, the outside of the grain is either bonded to the case, or is otherwise inhibited from burning. Burning, therefore, occurs only on the internal surface of the charge. A simple tubular charge burns with gradually increasing surface and therefore with gradually increasing release rate of gas. In order to achieve uniform release rate more complicated shapes are employed. Two such shapes are shown in Fig. 19.6 and are known as star centre and clover leaf charges. In each of these the initial burning area is equal to the outside area of the charge, so that the burning area remains essentially constant. Sometimes more than one composition may be employed in order to achieve suitable burning rates. Some allowance must also sometimes be made for increased burning speed in the initial stages of combustion due to the erosive effects of the products of combustion passing along the initial narrow channel of the charge.

Clover leaf   Star centre
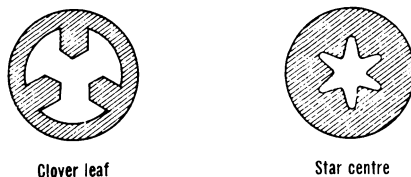
FIG. 19.6. Rocket charge sections.

A list of missiles using solid fuel rockets is quoted from Daboo in Table 19.3.

In the design of a charge for a rocket the quantities given are the expected total weight of the rocket, the maximum acceleration which the charge may give and the time for which this stage of the rocket should burn. The last two factors will determine the ultimate speed of the rocket. The maximum pressure for which the motor body is to be designed will also be given.

From the time of burning and the known pressure, together with the rate of burning equation for the selected propellant, the web thickness is calculated. This gives the size and cross-sectional area of the grain, assuming that it is radial burning, probably with a star centre. The total thrust required divided by the specific impulse gives the weight of the charge. As the cross-section is known the length of the charge can then be calculated. In actual practice, calculations are much more complicated, as they must allow for inefficiencies in the system and for air resistance and must also be carried out for various ambient temperatures which may

TABLE 19.3   *Missiles with Solid-fuel Rocket Propulsion*

Role	Range (km)	Launch weight (kg)	Designation	Propulsion
Air-to-air	3-6.5	50-200	Fireflash	Wrap-round separating boost. No sustainer.
			Firestreak Sparrow	Internal boost. No sustainer.
			Falcon	Internal boost-sustainer.
Surface-to-air	5-10	50-200	Seacat	Internal boost-sustainer.
	16-24	500-1500	Terrier	Tandem separating boost. Internal sustainer.
			Nike–Ajax	Tandem separating boost. Internal liquid-propellant rocket sustainer.
			Hawk Tartar	Internal boost-sustainer.
	32-48	2000-2500	Seaslug Thunderbird	Wrap-round separating boost. Internal sustainer.
	64-160	2000-5000	Nike–Hercules	Tandem separating boost. Internal sustainer.
			Bloodhound	Wrap-round separating boost. Ramjet sustainer.
			Talos	Tandem separating boost. Ramjet sustainer.

Air-to-surface	5–11	250–500	Bullpup	Internal boost. No sustainer.
			Nord A.S. 30	Internal boost-sustainer.
	1600–3200	5000–10 000	Skybolt	Ballistic missile.
Surface-to-surface	1·5–5	10–100	Vigilant Dart	Internal boost-sustainer.
	16–32	500–1500	Lacrosse	Internal boost. No sustainer.
	80–160	5000–7500	Sergeant	Single-stage ballistic missile.
	800–3200	7500–15000	Matador Regulus	Separating boost. Turbojet sustainer.
			Triton	Separating boost. Ramjet sustainer.
			Polaris Pershing	Two-stage ballistic missile.
	8000+	25 000–50 000	Snark	Separating boost. Turbojet sustainer.
			Minuteman	Three-stage ballistic missile.
High-altitude sounding rocket	(Height up to 160 km)	1000–2000	Skylark	Single-stage vehicle.
Satellite launcher	(Payload up to 100 kg)	15 000–20 000	Scout	Four-stage vehicle with single solid-propellant motor in each stage.

occur during use. Moreover, the burning pressure is probably not originally quoted, but deduced from consideration of its effect on the size and design of the motor itself.

Such a charge must in use perform regularly and give constant thrust. Should, for any reason, a slight increase in pressure in the chamber occur, two opposing factors operate:

1. The gases flow out from the chamber through the nozzle at an increased rate.
2. Gases are produced more rapidly by the propellant because of the increased pressure.

It can be shown that if the pressure index of the propellant exceeds 1 the rate of gas increase by factor 2 exceeds the rate of gas loss by factor 1, so that the pressure builds up in the motor, which finally explodes. Quite apart from such an extreme case, a low pressure index in the propellant is desirable so that irregularities in burning are quickly smoothed out with the least effect on rocket performance. It is for this reason that platonising agents mentioned on p. 181 are important, because they enable a very low pressure index to be achieved at ordinary operating pressures of the order of 14 MPa.

Power Cartridges

Special slow burning cool propellants can be used to generate gas under pressures suitable for the operation of mechanical devices. Perhaps the most important of these applications is in cartridge starting of jet engines for aircraft. The principles involved in this application of propellent explosives are illustrated in Fig. 19.7.
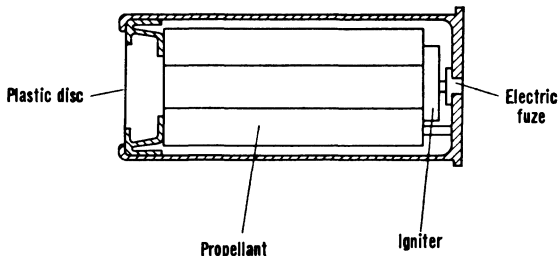
FIG. 19.7. Engine starter cartridge.

The propellant is usually either tubular or cigar burning, depending on the required time of operation. It is enclosed in a pressure chamber from which the gases are led through an orifice which controls the flow and regulates the pressure. A pressure relief valve is included for safety reasons. The hot gases from the orifice are taken to an impulse turbine which is geared to the rotor of the jet engine.

A jet engine has a compressor which provides compressed gas to a combustion chamber where the fuel is burnt. The hot gases from the combustion chamber pass through a turbine, which drives the compressor, and thence go to the jet. For the engine to be started the compressor must be driven above a critical speed, below which the power given by the turbine is insufficient to drive the compressor. The advantage of propellent cartridges for starting jet engines is that they enable the compressor and turbine to be brought to the critical speed in a matter of seconds. When this speed is reached fuel injection is provided into the combustion chamber and the engine is then capable of being run to its idling speed or above.

For civilian aircraft the facility for rapid starting is not important and cartridge operation is not often employed, particularly because it involves storing and handling explosives, even though the hazards of these explosives are those of fire and not of detonation. For military purposes, however, particularly for fighter aircraft which are best scattered on an airfield, a rapid start is of considerable importance. Therefore cartridge operated starters are much used for these aeroplanes. In Britain, development has been essentially with propellants based on ballistite, namely double base propellants of the solventless type, whereas in the United States composite propellants based on ammonium nitrate have proved more popular.

Electrically Actuated Devices

Electrically actuated devices (explosive motors) of small size are finding varied and increasing uses. Typically they contain a fusehead and in the larger sizes also a small charge of a propellent explosive such as blackpowder. This is sealed in a strong metal tube so that the finished device offers no explosive hazard. The firing of the fusehead can for example drive a captive piston a small distance outwards at the end of the tube. This in turn can be used to open or close a switch or valve or to work a guillotine cutter. These actuators have great reliability even after long

storage under adverse conditions and give strong rapid action from small electrical inputs. These properties make them of value in applications such as safety and security systems and in fire protection.

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Glossary of Common Terms and Abbreviations

Abel Heat Test. A quick routine test for demonstrating the absence from explosives of impurities causing low thermal stability (see p. 72).

A.D.C. Ardeer Double Cartridge Test. A test measuring the ability of cartridges of explosive to propagate over air gaps (see p. 68).

Advance. In mining or tunnelling, the distance by which the face or tunnel is moved forward by each round of blasting (see p. 138).

Airdox. A blasting device based on compressed air (see p. 89).

Amatol. A mixture of ammonium nitrate and trinitrotoluene.

Ammon gelignite. A nitroglycerine gelatine explosive containing ammonium nitrate as the main oxidising ingredient.

Ammonal. An explosive containing ammonium nitrate, trinitrotoluene and aluminium.

AN. Ammonium nitrate.

ANFO. An ammonium nitrate/fuel oil explosive.

Application time. In firing electric detonators, the time for which the electric current is applied (see p. 112).

B. and J. Bergmann and Junk. Test of stability (see p. 72).

Base charge. In a detonator, the charge of high explosive which makes the major contribution to the power of the device.

Boost. In rocketry, a motor which gives rapid acceleration for a short period.

Braid. To enclose in criss-crossing yarns of textile.

Break. In mining, a separation between strata or along a cleavage plane in coal or rock.

Break gallery. An experimental installation to assess the hazards of firing explosives in coal mines in the presence of breaks (see p.80).

Bridge wire. The fine wire in an electric detonator which is heated by the firing current.

Brisance. The shattering power of an explosive.

Briska detonator. A detonator in which extra power is achieved by extremely heavy pressing of the base charge.

Bulk strength. The strength per unit volume of an explosive, usually expressed as a percentage of the strength per unit volume of blasting gelatine.

Burden. In blasting, the shortest lateral distance between a borehole and a free face.

Bursting time. In firing electric detonators, the time between the application of the electric current and the explosion of the detonator (see p. 112).

Cap. A metal shell with pyrotechnic filling, such as is used in small arms ammunition for causing a mechanical blow on the outside of the shell to ignite the propellent charge inside. In the U.S.A. detonators are known as blasting caps.

Carbamate. Symmetrical diethyldiphenylurea.

Cardox. A metal tube device using carbon dioxide to produce a blasting effect (see p. 89).

C.D.B. Cast Double Base Propellant (see p. 174).

C.E. Composition Exploding. Tetryl, usually in the form of a pellet.

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Centralite. Symmetrical diethyldiphenylurea.

Cigar burning. In propellants, the burning of a cylindrical charge from one end only, the other surfaces being inhibited.

C.-J. Chapman Jouget (see p. 19).

Clearing Test. A test of the speed of solution of nitrocellulose in nitroglycerine (see p. 74).

Composite propellant. A propellant based on an oxidising salt and an organic fuel/binder.

Cordtex. British trade name for detonating fuse.

Corning. In blackpowder manufacture, the stage of the process which produces uniform spherical grains.

Counter. In fuse manufacture, to wind on textile yarns in a direction opposite to a previous spinning process.

Crimping. Squeezing a metal tube round a plug, fuse, or similar body to secure the latter firmly.

DDNP. Diazodinitrophenol (see p. 97).

Deflagrating explosive. An explosive which burns rapidly but does not detonate.

Deflagration. In high explosives, a relatively slow decomposition accompanied by fumes but not normally by flame.

Delay detonator. A detonator in which a time lag is introduced between application of the firing current and explosion of the detonator.

Detonating fuse. A fuse with a core of detonating explosive.

Detonation. An explosion process of high speed involving a sustained shock wave.

Detonator. A metal tube containing a primary explosive used for initiating a secondary explosive.

Double base propellant. A propellant based on nitrocellulose and nitroglycerine.

Drift. In coal mining, an underground tunnel through stone.

Electric detonator. A detonator for firing by electric current. The term does not normally include delay detonators.

End spit. The flash of burning material ejected from safety fuse when burning reaches a cut end.

Eq.S. Equivalent to Sheathed. The original name for Group P3 Permitted Explosives.

Excitation time. In firing electric detonators, the interval between the application of the current and the firing of the fusehead (see p. 112).

Explosion. A liberation of energy sufficiently sudden to cause dynamic stress to the surroundings.

Explosive. A chemical, or mixture of chemicals, which can react so rapidly and with such liberation of energy that there can be damage to the surroundings.

Explosive motor. A device in which explosive is completely enclosed and which on operation causes a mechanical movement as of a piston (see p. 195).

Exudation. In nitroglycerine gelatine explosives, a liberation of nitroglycerine following breakdown of the gelatinous base.

Fall hammer test. A test of the sensitiveness of explosives to impact using a weight which falls vertically (see p. 69).

Fizz zone. In the burning of propellants, the zone in which the solid propellant is converted to gaseous intermediates (see p. 182).

Flame zone. In the burning of propellants, the final stage in which gaseous intermediates react with the production of a flame (see p. 182).

Flash past. In assemblies such as delay detonators and military fuzes the possibility of an igniting flash by-passing a delay element.

Foam zone. In the burning of propellants, the initial stage of partial gasification (see p. 182).

Free face. In blasting, a face of rock or coal approximately parallel to the line of boreholes (see p. 138).

Fulminating compound. An early term, applied to mixtures of chemicals usually containing silver and used essentially for pyrotechnic purposes.

Fume. In mining, the gaseous products of an explosion.

Fuse. A cord for transmitting explosion from one site to another.

Fusehead. Ignition element for an electric detonator.

Fuze. Military device for initiating an explosive charge.

Gaine. An intermediate booster charge used between a detonator and an insensitive high explosive.

Gallery. Equipment for firing explosives into incendive mixtures of methane and air.

Gasless delay detonator. Original name for modern delay detonator.

Gassy coal mine. A mine in which methane may be present; also known as a safety lamp mine.

Gelatine. An explosive which is a jelly of nitroglycerine containing nitrocellulose, usually with oxidising salts and solid fuel dispersed in it.

Gelignite. Originally a gelatine explosive containing potassium nitrate as oxidising material. Now often applied to any gelatine.

Grain. A unit of propellant powder.

Guncotton. Nitrocellulose containing more than $12\cdot6\%$ of nitrogen.

Heat Test. A rapid stability test depending on detection of traces of products of decomposition of an explosive at an elevated temperature. In Britain this usually refers to the Abel Heat Test.

Hess Test. A German test for brisance (see p. 73).

High explosive. Literally any explosive which detonates. In practice, the term is usually confined to explosives which do not normally burn to detonation but which require a detonator for use.

High tension detonator. An early form of detonator which required a voltage exceeding 36 volts to fire it (see p. 107).

HMX. Cyclotetramethylenetetranitramine.

Hydrox. A steel tube device using low temperature gas produced from a chemical cartridge for producing a blasting effect (see p. 89).

Igniter cord. A cord for igniting safety fuse.

Induction time. In firing electric detonators, the time between the breaking of the fuse wire and the detonation of the base charge (see p. 112).

Initiating explosive. An explosive which when lit by a flame immediately detonates.

Instantaneous fuse. A fuse which propagates by burning at high velocity.

Kast Test. A German test for brisance (see p. 73).

Lag time. In firing electric detonators, the interval between the application of the current and the breaking of the bridge wire (see p. 112).

L.E.D.C. Low Energy Detonating Cord. A detonating fuse with a core charge too low to enable it to be used reliably for initiating high explosives (see p. 124).

Long wall mining. In coal mining, a method of working in which the coal is won along a face 100 to 200 m long.

LOX. Liquid Oxygen Explosive (see p. 59).

Mill cake. In blackpowder manufacture, a product taken from the edge runner mills.

Millisecond delay detonator. A short delay detonator.

Moderated. In propellants, implies the presence of a surface coating to the grain which slows down the initial rate of burning.

NC. Nitrocellulose.

NG. Nitroglycerine.

NS gelignite. A nitroglycerine gelatine explosive containing sodium nitrate as its main oxidising ingredient.

Opencast mining or strip mining. Obtaining coal or ore which is near the surface by removing the overlying soil and rock to expose the coal or ore for direct recovery.

Ordnance. The larger size military guns and mortars.

P1. The first and strongest class of Permitted Explosive.

P2. Originally called sheathed explosives, consist of P1 explosives enclosed in a sheath to give increased safety.

P3. Class of Permitted Explosives for general use with instantaneous detonators.

P4. Class of Permitted Explosives particularly for ripping with short delay detonators.

P5. Class of Permitted Explosives particularly for firing with short delay detonators in solid coal.

Paste. In double base propellant manufacture, the initial mixture of guncotton and nitroglycerine.

Pentolite. A mixture of TNT and PETN.

Permissible Explosive. The American equivalent to British Permitted Explosive.

Permitted Explosive. An explosive which is authorised for use in gassy coal mines.

PETN. Pentaerythritol tetranitrate.

Phlegmatise. To add a proportion of oil or other ingredient to render an explosive insensitive.

Picrite. Nitroguanidine.

Pillar and stall mining. A method of mining in which pillars are left to support the roof.

Plain detonator. An open detonator with no means of ignition attached.

Platonisation. In propellants, the addition of ingredients to produce a low pressure index over a working range of pressures.

Powder. A generic name for a propellent explosive.

Presplitting. A technique of blasting which gives accurate finished contours (see p. 148).

Press cake. In blackpowder manufacture, a cake taken from the presses.

Pressure index. In propellants, the variation of burning speed following changes in pressure (see p. 180).

Prill. An absorbent spherical form of a product, particularly ammonium nitrate.

Primary explosive. An alternative name for an initiating explosive. A flame causes the explosive to detonate immediately.

Primer. High explosive charge used to initiate other high explosive.

Priming charge. In detonator manufacture, the charge of initiating explosive.

Propellant. An explosive which normally burns and does not detonate.

Propellent. Adjective implying the possession of a propulsive effect.

RDX. Cyclotrimethylenetrinitramine.

Reaction time. In firing electric detonators, the time between the ignition of the fusehead and the explosion of the detonator (see p. 112).

Ripping. In coal mining, the removal of stone after recovery of coal to produce a road of normal size (see p. 143).

Safety fuse. A fuse which propagates by slow burning.

Safety lamp mine. Alternative name for gassy mine, implying possible presence of methane.

Secondary blasting. A process of breaking, with explosives, boulders from an initial blast which are too large for immediate handling.

Secondary explosive. Alternative name for high explosive indicating that the explosive does not burn to detonation but is detonated by suitable devices.

Semi-gelatine. An explosive containing nitroglycerine gelled with nitrocellulose, but in quantity insufficient to fill the voids between the salt and combustible particles and thereby produce a gelatine.

Shaped charge. An explosive charge designed to produce specific effects by the inclusion of a re-entrant conical or V shape usually lined with metal.

Shock wave. A pressure wave of high intensity characterised by a very rapid initial increase in pressure followed by a slow falling off.

Short delay detonator. A delay detonator with time interval between individuals of the series of 25 or 50 ms.

Single base propellant. Propellant based on nitrocellulose without the inclusion of nitroglycerine.

Slurry explosive. An explosive made by sensitising a thickened aqueous slurry of oxidising salts (see p. 55).

Small arm. A gun or rifle of up to about 2·5 cm in calibre.

Solid coal. Implies coal which is being worked without the provision of a free face by undercutting or similar means.

Solvent type propellant. A double base propellant in which solvent is used to assist the gelatinisation of the nitrocellulose.

Solventless double base propellant. A double base propellant in which gelatinisation is effected by mechanical means without the addition of solvent.

Spalling. In explosives technology implies the breaking off of a scab of material from a free face as a result of the reflection of shock waves (see p. 135).

Special gelatine. A gelatine explosive in which the main oxidising ingredient is ammonium nitrate.

Spin. In fuse manufacture, to wind on a spiral of textile yarns.

Stemming. The insertion, into the end of a borehole, of clay or other material which will resist the pressure of the explosive when the latter is fired.

Streaming velocity. The velocity of the products of detonation in the direction of travel of the detonation wave.

Strip mining. *See* Opencast mining.

Sustainer. In rocketry, a slow burning motor to produce a continued thrust.

TNT. Trinitrotoluene.

Torpedo friction test. A test of sensitiveness to impact and friction (see p. 70).

Triple base propellant. A propellant containing nitroglycerine, nitrocellulose and Picrite.

Tun dish. A large unstirred cylindrical vessel used for slow processes of steeping or steaming.

Undercutting. In coal mining, the production of a free face by cutting out mechanically the lowest 10 to 12 cm of a seam (see p. 142).

VOD. Velocity of detonation, usually measured in metres per second.

Web thickness. The distance of travel of a burning surface in a propellent grain to give complete combustion.

Wedge cut. A method of tunnelling, etc., in which a free face is first produced by blowing out a wedge of rock.

Weight strength. The strength per unit weight of an explosive, usually expressed as a percentage of the strength per unit weight of blasting gelatine.

Zapon. A solution of nitrocellulose used in fusehead manufacture.

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