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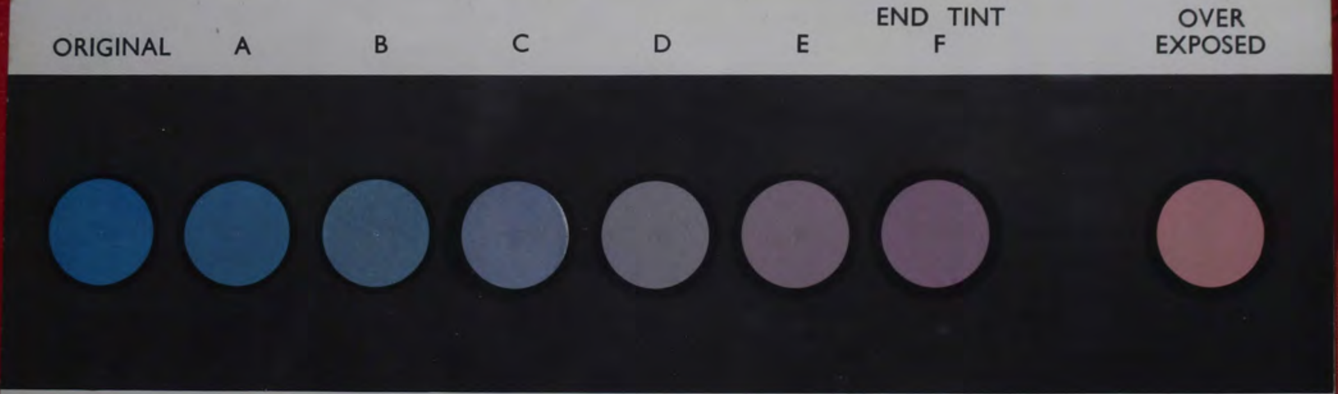

MATCHING WITH THESE TINTS TO BE CARRIED OUT IN DAYLIGHT.

INTERVAL BETWEEN EACH TINT REPRESENTS 1/6 OF THE TIME OF TOTAL CHANGE FROM ORIGINAL TO TINT F.

FIG : 16.6.

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26
Manuals
1887

TEXT BOOK

OF

EXPLOSIVES

USED IN THE SERVICE

1938

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MATCHING WITH THESE TINTS TO BE CARRIED OUT IN DAYLIGHT.
INTERVAL BETWEEN EACH TINT REPRESENTS 1/6 OF THE TIME OF TOTAL CHANGE
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FIG: 16. 6.

By Command of the Army Council,

H. J. Creedy

THE WAR OFFICE,
7th December, 1938.

PREFACE

This volume, being a " Text-Book", presents general principles rather than an exact description of details, which would properly be found in a " Treatise ". A fair knowledge of both chemistry and physics is assumed, but a short glossary of terms is included in Appendix III. Appendix V gives the physical properties of relevant chemicals and Chapters VI to XI, inclusive, refer to matters of a purely chemical nature, and treat of the more important raw materials and intermediates which are used in the manufacture of explosives.

This volume is based on lectures delivered at the Advanced Class Course at the Military College of Science, Woolwich.

The present work is based on the 1925 edition of the Text Book of Explosives, but has been re-arranged and brought up to date. Section C (Chemicals) is new, as are the descriptions of the calorimetric and 100 per cent. surveillance tests for cordites in Chapter XVI.

The large (kilogram) calorie is used for purposes of illustration throughout the book, and is denoted by the symbol " K." Physical constants are, as far as possible, drawn from Kaye and Laby's Tables of Physical Constants, 1936.

The conventional ring formula of Kekule is taken to illustrate the molecular constitution of benzene.

Flow diagrams are used freely ; these summarize concisely the general chemical and physical processes in explosives manufacture.

Illustrations are numbered consecutively throughout each chapter, the number of the latter being placed immediately before the number of the illustration, thus :

Fig. 2.1 is the first Figure in Chapter II.

The tables are lettered alphabetically throughout each chapter, the letter in each case being preceded by the number of the chapter, thus :

Table 4.A.

The term " shock of discharge " is used as being familiar, though it is recognized that the phenomenon so designated is a rapid acceleration and not a " shock ".

In the glossary of terms (Appendix III) the definitions given are only intended to apply to the terms in the sense in which they are used in this book.

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A.—GENERAL

CHAPTER I

INTRODUCTION

DEFINITION OF AN EXPLOSIVE—THERMO-CHEMISTRY OF EXPLOSIVES

Burning—Explosion—Detonation

An explosive is a substance whose function is to exert a sudden intense pressure on its surroundings when suitably initiated. This pressure is developed by the decomposition of the explosive into gas, with a simultaneous liberation of heat.

The criteria of an explosive are thus :

(i) Potential energy in view of its chemical constitution, which is independent of external agencies.

(ii) Formation of gaseous products with simultaneous liberation of energy.

(iii) Rapid decomposition when suitably initiated.

Explosion is in many cases analogous to the burning of a combustible substance in air or oxygen. Ordinary burning of a combustible in the air can take place but slowly, for the products of combustion must be swept away before the necessary oxygen can come into contact with the burning surface. In explosives, however, the oxygen is self-contained, and the explosion may take place under the most confined conditions, being quite independent of any material outside the explosive itself.

In some cases explosion is solely due to the simple decomposition of an unstable substance into its constituent elements. Thus lead azide gives lead and nitrogen by its decomposition :

$$\underset{\text{Lead azide}}{PbN_6} \rightarrow \underset{\text{Lead}}{Pb} + \underset{\text{Nitrogen}}{3N_2}$$

By the choice of explosive chemical compounds, by mixing them in suitable proportions, and by the modification of their physical forms, the velocity of the explosive process can be controlled to meet requirements of a widely differing nature. It may be made to take place at speeds of a few cms. a second, or it may be caused to rise to velocities of the order of 9,000 metres a second.

Such a rapid explosion as this is known as " detonation ", and explosives which can be " detonated " are called " high explosives ".

An explosive may consist of a single chemical compound, a mixture of two or more such compounds or a mixture of combustible elements with oxygen bearing compounds and further may be :

1. *Gaseous*, as in the case of the petrol vapour and air mixture (in the proportions required for explosion) used as a source of energy in I.C. engines.

2. *Liquid.*—Example, nitroglycerine.

3. *Solid.*—Example, picric acid or trinitrotoluene.

The above remarks apply to normal temperatures ; for the liquid nitroglycerine may be frozen and the solid picric acid may be melted.

Some explosives used in the service are of a horny and flexible consistency (*e.g.* cordites) ; others are rigid solids, and some are used in the form of crystals, granules or powder. In general, efforts are made to obtain them in as dense a form as possible, as this provides a maximum store of energy in the minimum space.

The explosive effect depends on two causes :

1. A very rapid liberation of gaseous matter (whose volume is very many times greater than that of the explosive) ; and

2. A simultaneous evolution of great heat.

The first generates a high gas pressure, which, enhanced by the expansive effect of the second, may become as high as 300 tons a square inch.

As a result of the pressure generated, surrounding solid matter may be ruptured and its fragments projected at great velocities.

Unless both the above-mentioned causes function simultaneously, chemical decomposition falls short of being an explosion. Thus :

(*a*) Ammonium carbonate can be decomposed into products which are entirely gaseous, but this entails an absorption of heat, and no explosion takes place.

(*b*) Magnetic oxide of iron (forge scale), if mixed in molecular proportions with finely divided metallic aluminium, and ignited by being brought to a fairly high initiating temperature, will evolve intense heat :

$$3Fe_3O_4+8Al \rightarrow 4Al_2O_3+9Fe+740K.$$

There is no evolution of gas, and so no explosion, but the mixture, which is known as " thermit," has been used commercially for welding and in the service for incendiary purposes. Temperatures of 2,500° C. can thus be obtained in a closed mould. All metals, with the exception of tungsten (M.P. 3,060° C.), tantalum and molybdenum, are melted before this temperature is reached.

Contrast with (*a*) and (*b*) above the following:

(*c*) Nitroglycerine burns quietly if ignited in small quantities, but it can be detonated by impact, friction or other suitable stimulus:

$$4C_3H_5(NO_3)_3 \rightarrow 12CO_2+10H_2O+6N_2+O_2.$$

Not only is it entirely resolved into gaseous products and all its carbon content burnt to carbon dioxide (which causes a maximum evolution of heat), but there is actually a surplus of free oxygen liberated. Very few explosive compounds, however, contain enough oxygen for their own complete combustion. The use of nitrogylcerine unmixed with other substances is somewhat curtailed by its liquid nature and extreme sensitiveness to shock of any kind, but it is largely used in the service as a constituent of the cordites, and also in blasting gelatine and dynamites.

Thermochemistry.

The formation of a chemical compound from its elements is associated with an absorption or liberation of heat, which is known as the *heat of formation* of the compound. Compounds are termed *endothermic* or *exothermic*, according as heat is absorbed or given out in their formation. When the reverse of combination takes place, for instance when a compound breaks down as in explosion, the heat change is reversed. Thus, when an endothermic compound is resolved into its constituent elements, the amount of heat which is evolved or absorbed, as the case may be, is equal to the heat of formation of the compound, but with the sign reversed.

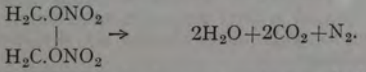
Thus:

$$\left.\begin{array}{l} 2C+O_2 \rightarrow 2CO+2\times26{\cdot}1K \\ C+O_2 \rightarrow CO_2+94.3K \end{array}\right\}\text{Carbon as diamond.}$$

$$2H_2+O_2 \rightarrow 2H_2O\left\{\begin{array}{l} +2\times58{\cdot}0K \text{ (water as vapour)} \\ \text{or}+2\times68{\cdot}4K \text{ (water condensed to liquid).} \end{array}\right.$$

The extra heat which is evolved if the water vapour is condensed (latent heat of vaporization) is not, in practice, available in explosions, whose temperature is well over 100° C. A "balanced" explosive, which contains sufficient oxygen to oxidize all the carbon to dioxide, is of value in making available the whole heat of formation of carbon dioxide and prevents the formation of the poisonous carbon monoxide.

Very few individual compounds are thus "balanced". Dinitroglycol is, however, an example. It decomposes thus:



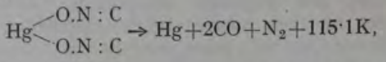
$$\begin{array}{c} H_2C.ONO_2 \\ | \\ H_2C.ONO_2 \end{array} \rightarrow 2H_2O+2CO_2+N_2.$$

When a compound breaks down on explosion, the heat generated is the difference between the heat of formation of the compound (whether positive or negative) and the sum of the heats of formation of the products of explosion.

Lead azide is an example of an endothermic compound which on explosion liberates heat due to its decomposition into its constituents :

$$PbN_6 \rightarrow Pb + 3N_2 + 110{\cdot}8K.$$

Fulminate of mercury, which contains oxygen, is another example of an endothermic compound. Its decomposition may be represented as follows :



$$Hg\begin{matrix} \diagup O.N:C \\ \diagdown O.N:C \end{matrix} \rightarrow Hg + 2CO + N_2 + 115{\cdot}1K,$$

i.e. the 62·9 Calories which are given out by the decomposition of a gram-molecule of fulminate are reinforced by $2 \times 26{\cdot}1$ Calories from the formation of 2 gram-molecules of carbon monoxide, thus giving a total heat liberation of 115·1 Calories.

Nitroglycerine is an exothermic compound, which gives out 99K (per gm. mol. understood) in its formation. The heat produced on explosion, therefore, is the difference between this quantity and the sum of the heats of formation of the various products.

The decomposition proceeds thus :

$$4C_3H_5(ONO_2)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2 + 1{,}351{\cdot}6K.$$

The total heat liberated may be shown as follows :

$$\begin{array}{lr} \text{Heat of formation of } CO_2 = 12 \times 94{\cdot}3 = & +1{,}167{\cdot}6K \\ +\text{Heat of formation of } H_2O = 10 \times 58{\cdot}0 = & +\ \ 580{\cdot}0K \\ \quad\text{(assumed as vapour)} & \\ -\text{Heat of formation of} & \\ \quad\text{nitroglycerine} \qquad = -4 \times 99 = & -\ \ 396{\cdot}0K \\ \hline \text{Total heat from 4 gm. mols. of N.G.} = & +1{,}351{\cdot}6K \\ \hline \therefore \text{Heat derived from 1 gm. mol. of N.G.} = & +\ \ 337{\cdot}9K. \end{array}$$

An explosive thus represents a compact store of energy. It cannot in the solid state be used as an efficient source of motive power in the ordinary sense of the word, though this use has frequently been suggested. The heats of combustion of ordinary fuels are from seven to nine times as great as the heats of decomposition of most explosives, but, whilst we get oxygen from the air, explosives carry their own supply, and consequently a much greater weight of explosive would be necessary to supply the energy given out by the combustion of a given weight of fuel. The rate of decomposition of explosives can, however, be controlled within certain limits, so that they can be used to drive projectiles from a gun, for launching aeroplanes from catapults or for blasting and demolitions, whether industrial or military.

Burning is a comparatively slow chemical action, which is accompanied by the evolution of heat and light. This action is usually one of oxidation, the combustible body being oxidised by the oxygen of the air. Oxygen is not, however, the only supporter of combustion. For example, magnesium powder will burn in nitrogen with the formation of magnesium nitride.

$$3Mg+N_2 \rightarrow Mg_3N_2+\text{Heat and Light.}$$

Chlorine gas will support the combustion of hydrogen, phosphorus and many of the metals.

Internal burning is the chemical reaction which occurs in a system containing the combustible material and the supporter of combustion in close association, as an intimate mechanical mixture, a solution or a single chemical compound. Since the system is independent of the rate of access of internal air, the reaction can proceed through the mixture at very high speeds. According to the speed and the character of the products of the reaction, internal burning can produce incendiary effects (as in thermite) or various degrees of violence of explosion or detonation.

Detonation is a chemical change, usually of the nature of internal burning, which proceeds very rapidly through the mass of an explosive and produces large amounts of heat and gases. Owing to the high speed of propagation, very high gas pressures are produced, and detonation is characterized by an intense local disruptive or shattering effect. The maximum velocity of detonation is quickly reached and then remains constant for a given explosive at a given density under constant confinement. Velocities of detonation vary from about 3,000 metres a second up to about 9,000 metres a second according to the nature of the explosive and its physical condition.

Explosion, as distinct from detonation, is a similar phenomenon but travels less rapidly through the explosive and does not produce the intense shattering effects characteristic of detonation.

CHAPTER II

THE FOUR CLASSIFICATIONS OF EXPLOSIVES—MODE OF DECOMPOSITION AS DETERMINED BY INITIATING EFFECT

Classification of explosives is essential, in order to arrive at a basis for framing rules for the protection of the community and of the workers employed in their manufacture and subsequent handling. Four distinct classifications may be mentioned :

The Explosives Act, 1875.
Magazine Regulations.
Service Classification.
Chemical Classification.

For the first two brief reference will suffice, but the latter will receive more detailed examination.

The Explosives Act embodies the Home Office Regulations for the licensing and manufacture of explosives and for the protection of the public and workers from accidents. It regulates, by means of licences, the quantities of explosive, the work to be performed, the number of work-people allowed in each building of a factory or magazine, and the distances to be observed between such buildings themselves and " protected works " such as dwelling houses, railways, public roads, etc., outside the factory or magazine. The inspection of factories is also ensured. It subdivides explosives into seven classes, for the purpose of reference with regard to their handling, storage and transport. Extracts of rules with respect to the transport of explosives may be seen posted at many railway stations. The Act is augmented from time to time as the necessity arises. (*See* Thompson, " Guide to the Explosives Act, 1875.")

Magazine Regulations adapt the relevant principles of the above to service conditions, and may be consulted in detail. These regulations classify explosives into groups numbered I to XIII, and lay down which groups must be kept apart and which may be stored together. Groups are allotted for storage in a " Magazine " (" a building or buildings with passage leading thereto, in which explosives detailed in Groups I and II must, and explosives detailed in Groups III and IV may, be stored, and which must be under *magazine conditions* ") or an " Explosives Store " (" a separate building or portion of such a building used for the storage of explosives "). Explosives stores should not be kept under magazine conditions except in so far as is laid down in Magazine Regulations, Part I, 1934, paragraph 178. Explosives in Groups V to XIII—except those specially stored as detailed in paragraphs 188 and 189—must, and those in Groups III and IV may, be stored in an explosives store.

Section VIII of Magazine Regulations defines "magazine conditions" in detail. Division into groups is based on the following principles :

Explosives of a sensitive character, requiring special precautions in storage and handling to obviate spark or friction, must be stored in a magazine. High explosives and propellants in bulk (not included in Groups I or II) and propellant charges may be stored in an explosives store, but are preferably stored under magazine conditions. Other explosives and ammunition must be stored in an explosives store.

When possible, ammunition and explosives are stored strictly by groups, each group in a separate building ; and, as far as is practicable, each type of ammunition or explosive is kept together so that buildings are completely filled with one type rather than with several.

Service classification divides explosives into three main categories, according to military usage ; two of these categories lend themselves to further subdivision :

1. Propellants (cordites, ballistite, N.C. powders, etc.).
2. High explosives.
   - (i) Bursting charges (lyddite, trotyl, amatols, etc.).
   - (ii) Intermediaries (picric powder, composition exploding, etc.).
   - (iii) Initiators (mercury fulminate, lead azide, etc.).
   - (iv) Demolition and mining charges (guncotton, etc.).

(3) Miscellaneous.
   - (i) Smoke producers.
   - (ii) Light producers.
   - (iii) Fog signals.
   - (iv) Incendiary compositions, etc.

To the above may be added :

4. Gunpowder.

1. *Propellants.*

These are required to explode at a moderately slow speed comparable with that of rapid combustion. This is designed to produce a sustained high pressure but one that never becomes unduly high and liable to overstrain the gun. Propellant charges of cordite or other explosive are made up from sticks, tubes or flakes of the explosive substance ; and the proper dimensions of these are calculated so as to give the correct speed of burning. This has to be adjusted with the greatest care, and the explosive made of such a physical form as to ensure that burning takes place from layer to layer and that sudden increases of pressure in the chamber are avoided. A sudden pressure would either burst the gun or seriously damage the bore. It is also important that the temperature of explosion should not be excessive. High temperatures lead to a rapid erosion of the bore, with consequent inaccurate shooting. As the nitroglycerine content of a propellant of the cordite type is increased, so is the temperature of explosion.

2. *High explosives.*

High explosives are required to produce a great disruptive effect by their explosion when suitably initiated. They must not, however, be unduly sensitive to shock or friction; for they must be safe in manufacture, transport and storage, and further, as shell fillings, must be able to withstand the shock of discharge without being affected. The great shattering power of these explosives is due to the speed with which the detonation wave travels through them. If the maximum disruptive effect is desired, it is generally better to use a single chemical compound, rather than a non-homogeneous mixture. Homogeneous mixtures, in which one ingredient is actually dissolved in another, may give a very high disruptive effect, especially when the mixture is "balanced"; the violence may exceed that of a single chemical compound. Blasting gelatine is an example of this class.

It is a fallacy to suppose that, in detonating, high explosives "strike downwards". In general, equal pressure is exerted in all directions, but with such high velocities of explosion the inertia of the surrounding air, and of the expanding gases from the explosive, becomes an important factor. The effect on the air cannot be seen, and the total result is liable to be judged from that which is visible on the ground.

3. *Miscellaneous.*

Under this heading are included mixtures which are not strictly explosive, but which, on account of their nature, need similar precautions for their safe handling and storage. Their uses are sufficiently indicated by their names.

4. *Gunpowder.*

This is best grouped by itself owing to its varied uses.

Gunpowder was originally used as a propellant, but is now used in time fuzes, igniters, primers, tubes and blank ammunition, and as a burster for shrapnel and base ejection types of shell where it is neither necessary nor desirable for the shell to be broken up into small fragments.

Chemical classification.

From a chemical point of view explosives may be grouped into two classes:

1. Explosive chemical compounds.
2. Explosive mixtures.

1. *Explosive chemical compounds.*

Each of these consists of a single chemical compound, which on explosion breaks down into two or more substances of a simpler nature. This class may be further divided, and considered under two headings :

(i) *Compounds containing combined oxygen, which on explosion oxidizes the combustible elements in the compound.*

The oxygen is for the most part originally associated with nitrogen ; on explosion the latter is usually set free, the oxygen combining with the carbon and hydrogen of the compound to form oxides of carbon and water-vapour. Such organic nitrates (nitric esters) as nitroglycerine and nitrocellulose, and also the true nitro-compounds such as picric acid and trinitrotoluene, and some inorganic compounds (*e.g.* chlorates, perchlorates, ammonium nitrate, etc.), fall under this heading. It has been seen (Chapter I) that the products of explosion depend on the amount of oxygen available in the explosive, and that the latter may be even in excess of requirements, as in the case of nitroglycerine. Very little or no smoke results from the explosion of such a substance. More often, however, as in the case of trinitrotoluene, there is a deficit of oxygen. In this case the unoxidized carbon is set free, resulting in characteristic black smoke.

$$2C_7H_5(NO_2)_3 \rightarrow 7CO+5H_2O+3N_2+7C.$$

(ii) *Endothermic compounds in which the molecule is in a state of unstable equilibrium.*

In their formation energy has been absorbed ; on receiving a suitable stimulus, they break up explosively, giving up this energy in the form of heat. Lead azide belongs to this class of compound ; it does not depend on combined oxygen for the emission of heat energy. Mercuric fulminate is an endothermic sensitive compound containing combined oxygen ; its decomposition, together with that of lead azide, has been demonstrated in Chapter I.

2. *Explosive mixtures.*

This class may also be conveniently considered under two headings :

(i) *Explosive mixtures containing explosive compounds.* For example :

Cordites. }
Ballistite. } (Containing both nitrocellulose and nitroglycerine.)
Amatols. (Ammonium nitrate and trinitrotoluene mixtures.)
Cap compositions. (Mercuric fulminate, potassium chlorate, and antimony sulphide, etc., mixtures.)

A considerable range in properties can be obtained by the use of such mixtures, according to the purpose for which the explosive is intended. The maximum heat energy from an explosive is only obtained when all the combustible materials within it are completely oxidized. For this reason many explosive compounds are mixed with other explosive or non-explosive compounds, in order to compensate for an excess or deficit of oxygen content. Complete oxidation of carbon causes an absence both of smoke and of the highly poisonous carbon monoxide. The absence of poisonous gases may be very desirable in mining operations. Smoke, however, is required for such purposes as the location of shell bursts, when the use of a " balanced " explosive necessitates the use of a special smoke mixture. Blasting gelatine has been mentioned above as a " balanced " explosive ; picric powder is a second example of such a mixture. It is very easily ignited from a powder flash and burns rapidly to explosive violence. In many cases it is quite unnecessary to consider the question of oxygen balance, as it is often outweighed by other desiderata. In the cordites, for example, it is more important that the temperature of explosion should be kept low enough to avoid erosion, rather than that the maximum available energy should be obtained from the propellant. Mercuric fulminate is often mixed with potassium chlorate in order to increase the heat of explosion ; and antimony sulphide may also be added. The latter increases the flame effect necessary for ignitory purposes. Explosives may also be mixed for reasons of economy, to obtain greater or less sensitiveness, to obtain some special effect (*e.g.* smoke, light, etc.) or to obtain a convenient consistency either for the manufacturing processes or for subsequent application.

(ii) *Explosive mixtures of non-explosive substances.*

These consist of mixtures of one or more combustible substances with one or more oxygen-bearing compounds. Gunpowder (carbon, sulphur and potassium nitrate) is a typical example. The combustible substances are rapidly burnt in the oxygen supplied by the oxygen-bearing compounds. As the various materials are merely incorporated, they are of necessity somewhat separated ; the explosion of such mixture is comparatively slow and is less violent than that of most explosive compounds. Heat is evolved by reason of the heat given out in the formation of the oxides being greatly in excess of that required for the break-down of the oxygen bearing compounds. Liquid oxygen, being now an article of commerce, and obtainable in unlimited quantities from the air, has actually been used (in conjunction with charcoal) as an explosive. In spite of its very low temperature very violent results can be obtained by its means. This is due to the possibility of greater closeness of contact between the oxygen and the combustible than is obtained in a mixture containing solid oxygen compounds. It is not generally convenient for military purposes, but was used to some extent by the Germans during the Great War for mining operations.

The velocity of the explosion wave in a gaseous mixture of oxygen and carbon-monoxide in molecular proportions has been the subject of practical experiment. Four distinct stages have been observed :

1. Ignition. During which the velocity rises to that of explosion.
2. Explosion. At a uniform velocity of a few metres a second.
3. Transition. A period of rapid increase of velocity to that of detonation.
4. Detonation. At a uniform velocity of several thousand metres a second.

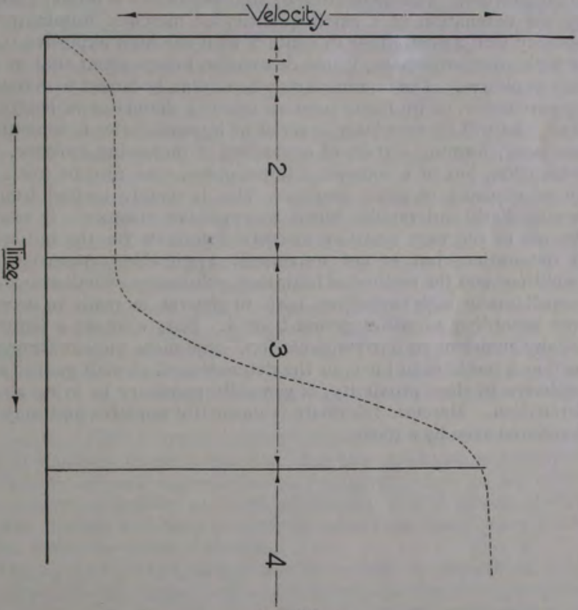


FIG. 2.1.

This may be more clearly shown on a diagrammatic velocity-time curve (Fig. 2.1) in which the respective stages are indicated by numbers corresponding with the above.

With solid explosives the transition period is quite short, or even practically absent, decomposition either continuing at the speed of explosion or passing rapidly to that of detonation, according to the composition of the explosive and the manner in which the explosion is initiated. Hence service classification of actual explosives may be defined according to the duration of the above periods on the velocity-time curve.

Propellants exploding in periods 1 and 2.

High explosives exploding in periods 1 to 4.

With initiators and intermediaries the first three periods are very short. Shell fillings and demolition, mine and similar charges are made to detonate in period 4 only, the requisite maximum velocity of the explosive wave having been reached within the initiatory system.

The explosion of propellants is initiated by a flash from an igniter of gunpowder. The detonation of high explosives is brought about by the detonation of a small quantity of mercuric fulminate (or possibly lead azide) either in contact with the high explosive itself or with an intermediary, whose detonation brings about that of the high explosive. The fulminate may be originally caused to detonate by percussion, or by flame from an ignitory detonator or length of fuze. As will be seen later, a series of intermediaries is sometimes necessary, forming a train of explosives of increasing violence. A detonation, but of a somewhat lower order, may also be initiated by an exploder of picric powder. This is readily ignited from a powder flash and rapidly burns to explosive violence ; it avoids the use of the very sensitive mercuric fulminate for the initiation of detonation, but is not universally applicable. According to conditions and the method of initiation, substances, whether modern propellants or high explosives, may, in general, be made to decompose according to either period 2 or 4. But, whereas a flame is usually sufficient to initiate explosion, some more violent stimulus, such as a mechanical blow, or the detonation of a small quantity of explosive in close proximity, is generally necessary to bring about detonation. Mercuric fulminate is unusually sensitive and may be detonated even by a spark.

CHAPTER III

HISTORICAL DEVELOPMENT OF EXPLOSIVES

The genesis of explosives is shrouded in obscurity ; the famous Greek Fire of the 7th century A.D. was probably of the nature of a firework, which no doubt created much surprise and consternation to an enemy until the novelty of the effect had worn off and it was discovered how little damage it could really encompass.

Opinions differ as to whether explosives were first known in Europe, Arabia or the Far East, and ancient documents concerning them are often purposely obscure and misleading. There seems, however, to be little doubt that a mixture of charcoal, sulphur and saltpetre, which closely resembled modern gunpowder in composition, was known throughout Europe early in the 14th century. This appears to have been used as a propellant at the Battle of Creçy, the projectiles being lumps of stone or iron. In these early times the naturally occurring saltpetre was the only known oxygen-bearing compound suitable for making an explosive mixture, and gunpowders with this as a main constituent held the field for nearly 500 years, being used both for propellant and disruptive purposes. "Shells" filled with such gunpowder were first tried in the 16th century. The first records of industrial "blasting" date from the 17th century. The shrapnel shell was invented by Lieutenant Shrapnel, R.A., in the late 18th century and was officially adopted in this country in 1803.

In the 17th century Glauber discovered *ammonium nitrate ;* but it was only in the Great War that this substance was destined to become of such supreme military importance, as an ingredient of modern explosives, although explosives similar in constitution to the amatols had been in commercial use for many years before 1914, under the name of *Rendite*.

Picric acid (*trinitrophenol*) was discovered by Woulffe in 1771. Its explosive properties were long undetected owing to its comparative insensitiveness, and for many years it was only used as a yellow dye. It is the earliest known example of an explosive nitro-compound in which the oxygen and combustible matter exist together in the same molecule. After its explosive properties began to be realized, Turpin in 1886 suggested compressing the material for use as a high explosive ; he was also responsible for its use in the form of a solid block, obtained by fusing the picric acid and casting it from the liquid condition. In this form (known in this country as *lyddite*) it still remains as a standard filling for certain shells. It was used in the war in South Africa, 1899–1902, but hardly justified itself in that campaign owing to the exploder system necessary for its complete detonation with certainty not having been fully worked out. It has a large energy content and, when properly initiated, detonates completely and with a high velocity. Its melting point is too high for it to be melted on a water bath, but it is quite stable at high temperatures of storage and so is in favour for the tropics.

Potassium chlorate was first prepared by Berthollet in 1786 and this, or one of the *perchlorates* discovered by Stadion in 1815, is a common constituent of modern mixed explosives.

Mercuric fulminate was produced by Howard in 1799, but its possibilities as an initiator were first exploited by Nobel, the inventor of dynamite, half a century later and were further worked out by Sprengel. It still remains as a standard initiator, although it deteriorates rapidly under hot conditions of storage. For this reason it may be replaced by *lead azide* in tropical countries. The latter was discovered by Curtius in 1890. It is claimed that much smaller quantities of it are necessary to cause complete detonation of high explosives, that it withstands high temperatures better and that unlike mercuric fulminate it does not become inert to flash when highly compressed.

In the 19th century the discovery of further explosives progressed rapidly, although many accidents, both in this country and abroad, acted as deterrents to their manufacture on a commercial scale.

Lead styphnate is now undergoing trials as an initiator in lieu of mercury fulminate.

Guncotton, a highly-nitrated form of *nitrocellulose*, was made by Schönbein in 1845 ; and *nitroglycerine* by Sobrero in 1846. Both these substances are nitric esters (organic nitrates) and not nitro-compounds, as their name would imply. The difficulties encountered in using the dangerously sensitive liquid nitroglycerine as a blasting explosive were partially overcome by Nobel in 1866 by absorbing it in the infusorial earth, Kieselguhr ; this takes up about three times its weight of nitroglycerine to form a plastic mass, which is comparatively safe to handle and a powerful explosive. It is called *dynamite*.

Blasting gelatine and *cordite*, both mixtures of nitrocelluloses and nitroglycerine, were brought out about 1878 and 1888 respectively. Cordite is now the standard propellant in this country. Several varieties exist and will be duly considered in a later chapter, but the compositions of the main types are :

	Cordite Mark I. Per cent.	Cordite M.D. Per cent.	Cordite W. Per cent.	Cordite S.C. Per cent.
Guncotton ...	37	65	65	50
Nitroglycerine ...	58	30	29	41
Mineral jelly ...	5	5	—	—
Carbamite ...	—	—	6	9

Cordite M.D. was introduced subsequently to Mark I, which, by reason of its high nitroglycerine content, gave a high temperature of explosion and caused much erosion in the guns firing it.

Cordites.

After the Great War, the War Office and the Admiralty initiated research into new types of propellant. The War Office required a propellant which should be free from flash and smoke. Cordite W is now being manufactured. Cordite W is essentially similar to cordite M.D., being incorporated in a similar manner. In cordite W carbamite is used instead of mineral jelly as a stabilizer. Cordite W is somewhat superior to cordite M.D., both as regards time of drying of the large sizes and as regards stability.

The naval propellant, cordite S.C. (*i.e.* solventless carbamite) is unique in that no solvents are needed in its incorporation. This has the great advantage of dispensing with a large acreage of drying stoves for the larger sizes and of speeding up production in case of need, there being no long time of drying, as for cordite M.D. or W.

The reasons why cordite S.C. was introduced into the naval service are :

1. Rapidity of manufacture.
2. Elimination of solvent.
3. Chemical stability. Carbamite is a powerful stabilizer and appears to prolong the service life of cordite almost indefinitely as far as safety is concerned. This permits of the use of wood cellulose as raw material, whereas it is necessary to use cotton for cordite M.D. or M.C.
4. Elimination of drying stoves.

Trinitrotoluene was discovered by Wilbrand in 1863. Being difficult to detonate and less sensitive than picric acid, it was only developed as a high explosive during the Great War, although it had been used previously as an intermediary. It has now become one of the most important high explosives in military use and is known in the service as trotyl or T.N.T. Its cost is only about one half that of lyddite and it can be safely and easily melted on a water bath and cast into shells. With a suitable exploder system it can be entirely detonated. It is a true nitro-compound and, not being an acid, does not readily form sensitive salts. It is, however, acted on by strong alkalies.

Trinitro-phenyl-methyl-nitramine or " tetranitro-methyl-aniline " is another nitro-compound and is of importance as an intermediary. It was first made by Mertens in 1877. It is invaluable in building up an exploder system, being readily detonated by a small charge of mercuric fulminate. It is, however, too sensitive, and too expensive for use as a shell filling, and cannot safely be melted and cast in large quantities. It is known in the service as tetryl, composition exploding, or " C.E."

During the Great War, in order to eke out the available supplies of T.N.T. for shell, grenade and bomb fillings, the *amatols* were introduced. These consist of intimate mixtures of T.N.T. and ammonium nitrate. They are comparatively insensitive and need a special exploder system to ensure their complete detonation. Various proportions are used, each amatol being designated by a pair of figures (*e.g.* 80/20—" eighty, twenty ") ; these represent the percentages of ingredients, the first figure always applying to the ammonium nitrate. Amatols represent a great economy in output of explosive, for the cost of ammonium nitrate is about one-quarter that of T.N.T. When efficiently detonated, 40/60 amatol is little less violent than T.N.T. alone. But 80/20 amatol has a lower rate of detonation and is almost smokeless, although it has a higher total energy content. Ammonium nitrate can be detonated by a sufficiently powerful impulse, but is not used alone as an explosive, being deficient in power.

From the foregoing brief review it will be seen that the majority of explosives mentioned are nitric esters or nitro-compounds, or else contain inorganic nitrates. Until quite recent years the naturally occurring nitrates of sodium and potassium have been the sole source of nitrates and nitric acid. The beds of sodium nitrate in Chile still remain the most important source for this country, and these produced two and a quarter million tons in 1920 ; but such natural resources cannot last indefinitely, and of necessity every country has, in turn, sought for some source of supply which has not to be sea-borne. The most obvious possibility of supply lies in the nitrogen of the air, and several methods are in use, which directly or indirectly convert this into nitric acid. Some of these will be considered later (Chapter IX).

Ammonia can be catalytically oxidized to nitric acid and hence converted into nitrates. The vast quantity of ammonia recovered from the destructive distillation of coal is thus a valuable source of nitrates. Of the world's production of nitrates and ammonia in 1920, 30·2 per cent. came from Chile saltpetre, 26·6 per cent. from ammonia recovery from the distillation of coal and 43·2 per cent. from synthetic methods.

The following figures give some idea of the tremendous output of the most important high explosives during the Great War (1914–1918) :

	Tons
Picric acid	68,511
T.N.T.	238,364
Ammonium nitrate	378,395

The construction and running of factories, and the amassing of raw materials (many of them necessarily sea-borne) to cope with the production of such unprecedented quantities of explosives, represents a stupendous task.

By far the greater quantity of explosives expended in the service are required for two main purposes :

1. The driving of projectiles from guns, howitzers, mortars and small arms. Explosives used for this purpose are called *propellants*.
2. Disruptive purposes, such as bursting shells, bombs, mines, etc., and accomplishing demolitions. Explosives most suited to these purposes are the ones that can be detonated ; these are called *high explosives*.

A propellant charge may vary in size from that necessary to drive an automatic pistol bullet weighing much less than one ounce, to that required for a large modern naval shell weighing three-quarters of a ton or more. Perhaps nothing so well illustrates the advance in the manufacture of ordnance and explosives as the comparison of the 800 yards range of Napoleonic artillery with that of over 22,000 yards of the naval guns at the Battle of Jutland. The German " Big Bertha " with its range of some 70 miles remains an extreme case even for the present day.

It is necessary to consider in some detail the main essential requirements of an explosive to be used for either of the above purposes.

ESSENTIAL REQUIREMENTS OF A PROPELLANT

1. *To give regular ballistics*, *i.e.* a regular rate of burning, and so a steady development of pressure. This can be obtained if the propellant :

(*a*) is uniform in composition ;
(*b*) burns at its surface only, and at a regular speed from layer to layer ;
(*c*) does not break up, giving a sudden change of surface area during combustion.

If these three conditions are satisfied, the rate of pressure development depends on the ratio :

$$\frac{\text{Surface area of the explosive.}}{\text{Volume of the explosive.}}$$

This ratio is adjusted to give correct speeds of burning by varying the shape and dimensions of the explosive charge.

2. *Not to cause erosion of the gun.*

Erosion results from :

(*a*) the friction of solid products of combustion ;
(*b*) surface hardening due to alternate heating and cooling, rendering the bore liable to surface disintegration ;
(*c*) the washing action of hot gases.

Cordite Mark I is more erosive than cordite M.D. because of its higher oxygen content causing a higher temperature of explosion.

3. *To be free from solid products of combustion.*

These cause smoke, which, besides disclosing the position of the gun, may hide subsequent targets. Fouling of the bore may also be caused, with the possible danger of ignition of the next charge from smouldering fragments of the previous round in a B.L. gun or howitzer. Solid products are formed by substances which are not volatile or which fail to be completely burnt. From gunpowder these are chiefly potassium carbonate and sulphide and any unburnt carbon. From propellants of the cordite type, unburnt hydrocarbon, derived mainly from the mineral jelly, is the chief solid product. Steam and nitrogen peroxide (NO_2) also occur in the smoke.

4. *To be free from muzzle flash and back flash.*

These are both caused by the ignition of the combustible gaseous products of explosion (hydrogen, carbon monoxide and small quantities of methane (CH_4)), either at the muzzle or on opening the breech, as the case may be. The former is likely to disclose the gun position, particularly at night, whilst the latter may be a source of danger of ignition of cartridges in the neighbourhood of the gun. They could be reduced by lengthening the gun or by raising the oxygen content of the propellant, but either of these courses is open to objection on other grounds. Various substances such as chlorides and oxalates or inert organic substances have been tried in conjunction with the propellant charge, to reduce the muzzle flash, either by cooling the gases below their temperature of ignition before they come in contact with the air or by altering their composition so that they are not in a suitable condition to ignite. Most flash reducers have a tendency to increase the smoke.

5. *To be stable for storage.*

This matter is discussed generally in Chapter XVI.

6. *To be stable for transport, i.e.* not too sensitive to impact or friction. Most modern propellants are satisfactory in this respect.

7. *To give the maximum propellant effect.*

This depends in part on the volume of gas, and on the quantity of heat evolved by the explosion of unit mass (1 gram) of the propellant.

If V = Number of cubic centimetres of gas evolved from the explosion of 1 gram of the propellant,
C = Number of gram-calories of heat evolved from the above.

Then,
$$\frac{V \times C}{1{,}000}$$

gives a rough figure of propellant effect, suitable for purposes of comparison. According to this:

Gunpowder gives 186.
Cordite M.D. gives 876.

Gunpowder (charcoal 15 per cent., sulphur 10 per cent., saltpetre 75 per cent.), originally used as a propellant, was eventually found to be quite unsuitable for this purpose. It gives most irregular ballistics, especially at high pressures, chiefly owing to the impossibility of regulating its rate of burning. A mechanical mixture, it remains porous and easily penetrated by hot gases, whatever efforts are made to compress or glaze it. Attempts were made to get better results by shaping the grains, perforating compressed blocks and varying the composition and moisture content ; but none of these was very successful, and charges generally broke up in burning, giving rise to sudden high pressures. A further great disadvantage is the large quantity of smoke evolved and the fouling left in the gun, more than half the products of combustion being solid.

Most of the faults of gunpowder were avoided by the introduction of colloidal smokeless propellants. These are readily obtained to fulfil the majority of the above requirements. They consist of mixtures of nitrocelluloses and nitroglycerine, incorporated together in various proportions, together with certain substances which increase their chemical stability. They comprise the various types of cordite and ballistite. Nitrocellulose without the addition of nitroglycerine is the standard American propellant and was introduced into this country during the Great War. This is in the form of short cylinders pierced with seven small longitudinal holes, and is known as " N.C.T." (nitrocellulose tubular). A small quantity of diphenylamine is added as a stabilizer. In all cases the final product is in a horny non-porous condition, having been gelatinized during manufacture with or without the aid of a volatile solvent, the bulk of which, if used, is removed in the final stages of manufacture.

ESSENTIAL REQUIREMENTS OF A HIGH EXPLOSIVE

The essential requirements of substances to be used for large disruptive charges (shell fillings, demolitions, etc.) may be conveniently considered separately from those of initiators and intermediaries, and will be taken first :

1. *To have a maximum shattering effect.*

This necessitates :

(*a*) a large volume of gas being liberated on detonation ;
(*b*) the evolution of a large quantity of heat ;
(*c*) a high velocity of detonation.

2. *To be highly insensitive to shock or friction :*

This is in order to be safe for transport ; and to withstand the shock of discharge and of penetrating armour plate when used as a shell filling.

3. *To be obtainable in a form of high density :*

This is in order to :

(*a*) have a large mass in a given space ;
(*b*) decrease sensitiveness ;
(*c*) avoid "set-back", which may cause incomplete detonation due to discontinuity of the explosive material ; or prematures, due to friction against the containing walls ;
(*d*) increase the rate of detonation.

4. *To have sufficient ease of detonation, i.e.* to be certain of complete detonation under the initiation of a suitable exploder system, which will itself safely withstand the shock of discharge.

This is in opposition to 2, necessitating a certain amount of compromise.

Difficulty was at first experienced in obtaining complete detonation with both lyddite and amatol shells of early type.

5. *To be stable for storage.*

This is discussed generally in Chapter XVI.

6. *To be free from reaction with the containing vessel.*

Certain explosives such as lyddite and the amatols tend to react with some metals with the formation of sensitive salts. The nature of the containing vessels must thus be chosen carefully in order to avoid this interaction, and suitable protective coatings applied if necessary.

ESSENTIAL REQUIREMENTS OF INITIATORS AND INTERMEDIARIES

1. *To rise rapidly to the maximum velocity of detonation.*

2. *To be detonated readily by the means in use, i.e.* percussion, flame or detonation of a neighbouring initiator.

3. *To be free from reaction with the containing vessel*, whereby either the latter, or the properties of the explosive may be injured.

Mercuric fulminate is satisfactory in copper sheaths, but lead azide is liable to interact with copper under damp conditions, and aluminium sheaths are used unless the sheath is provided with a watertight seal.

4. *To be stable for storage.*

Mercuric fulminate rapidly deteriorates in hot climates. Lead azide may for this reason replace it.

Gunpowder was the first explosive used for disruptive purposes, but, in addition to being an indifferent propellant, it is also a poor disruptive. It needs heavy confinement to produce any effect ; its energy content is low, as is also the rate at which its energy is liberated. It is very inflammable, and sensitive to friction and glancing blows, making a fabric container necessary for its protection in shell fillings. As a disruptive it is only used in certain cases where little violence is required.

Means of initiation.

It is important that the various methods of initiating the different types of explosion should be appreciated. A brief outline of the most important of these is given below. Further details, and their application to particular cases, may be sought in the Text-book of Ammunition.

Gunpowder is ignited very readily by a small flash; this is usually procured from some form of percussion cap enclosing some sensitive substance or mixture, which usually, although not necessarily, contains mercuric fulminate. The cap may be enclosed in a tube, fuze or cartridge case, etc., according to the purpoes for which it is required.

In some cases gunpowder may be ignited by a small wire raised to a white heat by an electric current; to facilitate the ignition, the wire may be surrounded with guncotton yarn or dust.

The flash from gunpowder ignited as above may be used to explode a further quantity of gunpowder (the igniter of a cordite cartridge, the magazine or the time ring of a fuze); or it may be used to ignite a picric powder exploder system in a lyddite shell. When ignited, picric powder develops sufficient violence to initiate explosion of the lyddite, but the degree of violence of the latter with such an initiatory system is somewhat less than that of complete detonation, especially with the smaller natures of the shell. Its advantage lies in the avoidance of the very sensitive mercuric fulminate in the initiating system.

To cause complete detonation, some more violent and sudden stimulus is necessary. A mechanical blow, the rapid burning of the explosive itself under confinement, or the detonation of another explosive in contact with the first, provide possible methods. Of these the last is usually the most practicable and convenient; the actual method used must be adapted to the sensitiveness of the high explosive and the manner in which the latter is used.

Wet guncotton for demolitions, etc., is detonated by means of a small primer of dry guncotton, which is itself initiated by a detonator containing a fairly large charge (*i.e.* as much as 2 grams) of mercuric fulminate, or a mixture of potassium chlorate and mercuric fulminate, which may be fired either electrically or by a flame from a length of fuze. Such a charge of fulminate as this could not safely withstand the shock of discharge from a gun; a much smaller quantity, on the other hand, would not serve to bring a modern shell-filling to complete detonation. For this purpose detonating fuzes and special exploder systems within the shell are necessary. The detonation of a very small quantity of mercuric fulminate initiates that of a small quantity of C.E. within the fuze. This detonation is picked up within the shell by exploder bags filled with loose C.E. or T.N.T., and the detonation of the latter suffices to detonate a filling of T.N.T. or lyddite. C.E. exploders are not, however, used with lyddite, as these two substances interact chemically to the detriment of the former.

For the more highly insensitive amatol fillings the above system requires still further reinforcement. The whole exploder system forms a train of detonating explosives, in which the detonation wave works up to its maximum velocity, passing on through the mass of the main high explosive at this velocity. The exploder bags must be tightly packed and each component part of the exploder system must be in close contact with the next ; any discontinuity in the form of an air gap must be avoided, as the detonating impulse rapidly falls off across such a gap. The detonator and various intermediaries must be well confined to obtain the maximum effect ; mercuric fulminate, if ignited in the open, may explode with no greater violence than gunpowder.

The properties and general principles of manufacture of individual explosives will be considered in later sections of the book.

B.—PHYSICAL AND CHEMICAL PROPERTIES OF EXPLOSIVES

CHAPTER IV

HEAT, GASES, PRESSURE AND TEMPERATURE OF EXPLOSION

Introduction.

In order to examine the purposes for which certain explosives may be most suitably employed, and in order to compare explosives with each other, there are a number of properties, both chemical and physical, which can be considered from both a qualitative and quantitative point of view. Of these :

(i) the heat of explosion,
(ii) the volume and nature of gases evolved on explosion,
(iii) the pressure produced by explosion,
(iv) the temperature of explosion,

will now be considered. Further properties will be dealt with in the next chapter ; and a tabulated list of physical data for explosives is given in Appendix II.

In the above " explosion " is, in general, intended to include " detonation ".

(i) *Heat of explosion.*

The heat evolved by the explosive decomposition of unit mass (1 gram) of an explosive gives an approximation of the total energy content ; this represents the difference between the quantity of heat evolved by the formation of the various products of the explosion and that absorbed in the formation of the original explosive. This quantity is by no means representative of the total useful work that an explosive can do ; much of the liberated energy cannot be turned to useful account, but is dissipated as heat and to a certain extent as light and sound.

To measure the heat of explosion, a weighed quantity of the explosive is exploded in a gas-tight metal bomb calorimeter, under standard conditions, the explosion being usually initiated by an electrically heated wire. The calorimeter is immersed in water contained in a vessel covered with heat-insulating material. The water is stirred mechanically, and its temperature recorded by an immersed thermometer reading to hundredths of a degree. The quantity of water being known, together with the water equivalent of the calorimeter, the heat evolved by the explosion can be calculated from the rise in temperature of the water.

The heat of explosion can also be calculated theoretically, when the composition of the products of explosion from a known weight of explosive has been determined.

(ii) *Volume and nature of gases evolved on explosion.*

A weighed quantity of the explosive is fired electrically within a "closed vessel." The latter consists of a massive metal bomb with special obturating arrangements. For safety, it is enclosed in a concrete building, the gear for firing the charge being operated from outside the building. Arrangements are made for drawing off the gases after explosion. Their volume is then measured at atmospheric pressure and a sample analysed. Any water-vapour formed is condensed, and from its weight the volume which it would occupy in the gaseous state can be determined. The experimentally measured volume of gas is that of "permanent" gases; the "total" volume of all the products of explosion in the gaseous state can also be computed. This "total" gas volume is of little value by itself, although a rough figure of "propellant effect" may be obtained, as explained in the previous chapter, by considering the product of the heat and the "total" gas volume, evolved from the explosion of the unit mass of the propellant.

(iii) *Pressure produced by explosion.*

In the case of slow-burning explosives (propellants), the pressure produced by explosion is also obtained from a "closed vessel" experiment. The pressure of the liberated gases is caused to act on the head of a piston working in a hollow cylinder. The piston crushes a small solid copper cylinder within the latter, and the amount the copper cylinder is crushed is an indication of the pressure. In some instruments a lead cylinder is used in the place of copper, but in either case the pressure is usually registered automatically by a stylus attached to the piston making a trace on a revolving smoked cylinder. As the speed of revolution of the smoked cylinder is known, the trace obtained represents a pressure-time curve.

The pressures measured as above much depend on the density of loading, *i.e.* the ratio of the weight of the explosive (in grams) to the volume of the "closed vessel" (in cubic centimetres), and on other physical conditions of the explosive, etc. For purposes of comparison, therefore, experiments with different explosives must be made under similar standard conditions.

It is quite impossible to measure the sudden dynamic pressure produced by a true detonation by any method involving the crushing of standard soft metal cylinders, as mentioned in former paragraphs, and even with slow-burning propellants such methods are at the best only approximate. The " total " gas volume gives some idea of the pressure likely to be exerted, but this again is very approximate, for the pressure is also a function of the temperature at which the gases are evolved and this cannot be determined without a knowledge of the specific heats of the gases ; these are not known with any certainty at temperatures as high as those of explosion.

It is hoped that modern research may produce a more satisfactory method of measuring pressures, based on the electrical properties of certain crystals when subjected to pressure. (Piezo-electric effect.)

In the meantime, with the Hopkinson pressure bar it is possible to measure with comparative accuracy the pressure set up in the immediate neighbourhood of a detonating explosive. This is not an absolute quantity, but depends on the way the explosive is " tamped " and the explosion initiated. For purposes of comparison, experiments must, as usual, be made under standard conditions.

At an earlier date rough tests were carried out for the comparison of explosives by means of the ballistic pendulum. This apparatus compared momenta given to a standard projectile by different explosive charges under standard conditions, but took no account of the period of time over which the explosive impulse acted on the projectile.

The Hopkinson pressure bar is now the standard instrument for determining pressures. Its principle is as follows :

If an explosive be detonated against or in the neighbourhood of the end of a cylindrical steel shaft, a wave of compression is transmitted along the rod with the velocity of sound in the steel (about 17,000 feet a second). Further, if the shaft be divided at a short distance from the end farthest from the charge, the opposed faces of the cut being carefully surfaced and held in firm contact, the compression wave passes this joint unaltered. Reaching the end of the shaft beyond the joint, the wave is reflected as a wave of tension, and the pressure at any section of the rod is the algebraic sum of the effects of the pressure wave and the tension wave when the front of the reflected wave has passed the surfaced joint ; the conditions are such that the entering tension wave tends to separate the small portion of the shaft (known as the " time-piece ") from the main shaft, while the tail of the compression wave tends to hold the time-piece on. As soon as the amplitude of the tension wave exceeds that of the compression wave, the time-piece is free to separate, the momentum trapped in it being the integral of the pressure-time wave which has passed the joining ; in other words the area enclosed between the pressure-distance curve and the time axis.

By varying the length of the time piece the shortest time-piece can be found which will effectively trap the bulk of the momentum which is given to the steel bar. Suppose this length be l inches. The time taken in seconds for the wave to travel twice the length of the time-piece is $\frac{2l}{12\times 17{,}000}$ or roughly $l\times 10^{-5}$ seconds. If the momentum given to the time-piece be W lb. foot-second units, then the average force which has acted on the bar is the rate of change of momentum of the time-piece, that is $\frac{W}{l\times 10^{-5}}$ or $\frac{W}{l}\times 100{,}000$ lb. wt.

The apparatus is shown in Fig. 4.1. and indicates the arrangement for detonating a gaine on the end of the steel shaft. The gaine is clamped firmly to a heavy steel base by means of a stout plate and bolts in such a manner that, on detonation, it exerts a blow on the end of the steel shaft, which is suspended as a ballistic pendulum.

The time-piece is attached to the further end of the shaft, firm contact being maintained by smearing the surfaced faces very lightly with vaseline. On delivery of the blow, the time-piece is projected and caught in a ballistic pendulum, adjusted so that the angle of swing does not exceed a few degrees. The momentum of the pendulum is then proportional to its linear displacement, which is recorded on a smoked glass plate by a needle fixed to a sprag attached to the bottom of the pendulum.

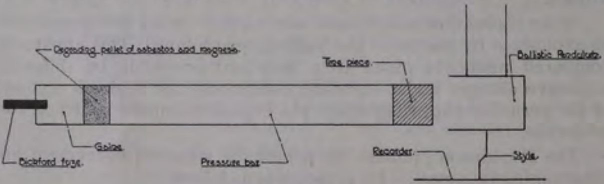


FIG. 4.1.

Determination of the pressure.

Let x = length of the record in inches.

$M+m$ = mass in slugs of the pendulum and time-piece, including one-third of the mass of the suspending wires (1 slug = 32·2 lb. mass).

T = time of oscillation of pendulum in seconds.

L = length of time-piece in inches.

Then the mean value of the pressure

$$P = 23{\cdot}8\,\frac{(M+m)x}{T.A.L.}\ \text{tons per square inch,}$$

where A is the area of explosive in square inches. By altering $M+m$, the value of the pressure corresponding to 1 inch of record may be varied ; thus, in order to minimize the labour of calculating the pressure, the weight of the pendulum can be adjusted so that the pressure per inch of record is some convenient number, *e.g.* 10 or 50 tons per square inch.

It is also evident that, by means of adjustment, the instrument may be used to investigate a very wide range of impulses and pressures.

For details of the work the reader is referred to the original papers of Bertram Hopkinson (Cambridge University Press, 1922, pp. 423 *seq.*).

The pressures actually developed reach a magnitude of hundreds of tons per square inch. No material could withstand the application of such stresses, and so a " degrading pellet " of asbestos and magnesia, which is scattered on explosion, is interposed between the explosive and the end of the bar. It is made of standardized material and degrades the blow. Typical measured pressures are in the neighbourhood of 60 tons per square inch, whilst those actually developed may rise to 300 tons per square inch, measured over a period of 1/200,000th second.

(iv) *Temperature of explosion.*

No direct method has yet been devised to measure this, the actual process of explosion taking place too quickly for any known method of observation. It can only be roughly estimated by calculation ; and for this two methods are available :—

(*a*) The product of the volume and pressure of a given mass of a gas is related to its absolute temperature. If the two former have been experimentally determined, the latter can be worked out.

(*b*) The temperature can be estimated when the heat of explosion (determined by the foregoing bomb calorimeter experiment) is known, provided that the natures and specific heats of the gases evolved are also known. Owing to the impossibility of, at present, determining the latter with any accuracy at such high temperatures as those of explosion, this method gives results which are widely at variance with those of the former method. It is, however, claimed that modern research has to a great extent accounted for these discrepancies.

Some experimental results obtained by Sir Andrew Aske for typical propellants are given below.

TABLE 4.A.

HEAT, GASES, PRESSURE AND TEMPERATURE OF EXPLOSION OF PROPELLANTS

Density of loading, 0·05.

Quantities evolved from 1 gram.

	Cordites.		Nitrocellulose propellant 100 per cent.
	Mark I.	M.D.	
Heat evolved (calories, with water liquid)	1·272	1·036	0·896
Permanent gases (c.c.)	678·0	781·8	814·7
Total gases (c.c.)	886·0	933·0	961·0
Percentage composition of total gas—			
CO_2	20·97	14·85	14·68
CO	26·53	34·87	35·63
H_2	13·52	18·95	20·01
CH_4	0·23	0·29	0·49
N_2	15·99	12·89	11·19
H_2O	22·76	18·15	18·00
Pressure (tons per square inch) ...	2·9	2·7	3·35
Temperature (estimated, ° C.) ...	5151°	3525°	3488°

The high percentage of inflammable gases, chiefly carbon monoxide and hydrogen, may be noted. It is these that cause muzzle and back-flash.

Many chemical equations are given in subsequent chapters illustrating the break-down of the various explosives. In all cases the simplest possible examples have been taken. Whenever an explosive containing carbon and oxygen explodes, both carbon monoxide and carbon dioxide will be formed (although, as a rule, only one of these appears in each of the above equations). It is almost impossible to predict the comparative proportions of the two gases, this being a function of the temperature of explosion as well as of the relative carbon and oxygen content of the explosive.

Table 4.B.
PROPERTIES OF HIGH EXPLOSIVES

Explosive.	Specific Gravity.	Density as applied.	Figure of insensitiveness (picric acid=100).	Heat value gramcalories per gram (water gaseous).	Volume of gases produced on explosion (c.c. per gram).	Power lead block test (picric acid=100).	Rate of detonation (metres a sec. at density).
Amatol 40/60	1·70	1·54	115	920	890	114	6,470 (1·55)
Amatol 80/20	1·71	1·25 to 1·45	111 to 120	990	900	120	4,620 (1·2) to 5,080 (1·5)
Ammonal	—	1·1	over 110	1,400	900	140	4,135 (1·07)
Baratol 80/20	1·86	1·75	101	910*	650*	85	5,000 (1·75)
Baratol 70/30	2·57	2·4	100	766*	380*	64	4,100
Cap composition (S.A.A.) ...	—	—	8	490	85	—	—
Detonating composition (" A " mixture)	—	—	6	650	115	—	—
Guncotton, dry	1·67	1·15	23	960	850	115	7,300 (1.2)
Guncotton, wet (13 per cent. water)	—	1·2	70 to 100	750	900	111	5,500 (1·1)
Lead azide	4·81	4·01	15 to 25	385	230	37	4,500 (3·8)
Lead styphnate	3·09	2·93	18	450	325	39	2,200 (1·1) to 4,900 (2·6)
Mercury fulminate	4·43	4·07	10	410	230	39	4,500 (3·3)
Picric acid (lyddite)	1·76	1·6	100	990	700	100	7,250 (1·63)
(C.E.) Tetryl	1·76	1·45 to 1·55	70	1,100	750	120	7,520 (1·63)
Trotyl (T.N.T.)	1·68	1·56	106 to 115	1,040	640	95	6,950 (1·57)

* Estimated.

CHAPTER V

VELOCITY OF DETONATION, SHATTERING EFFECT AND INSENSITIVENESS OF HIGH EXPLOSIVES

Introduction.

Further properties of explosives which it is necessary to examine are:

(i) Velocity of detonation.
(ii) Shattering effect.
(iii) Insensitiveness to impact or friction.

(i) *Velocity of detonation.*

One of the primary essentials of an explosive is that it should explode at a velocity that is in keeping with the object for which it is required. Velocities of explosion vary very widely, being chiefly influenced by:

(*a*) The chemical nature of the explosive.
(*b*) Its physical state.
(*c*) Its state of confinement.
(*d*) The method in which the explosion is initiated.

Cordite will burn rapidly if ignited in small quantities in the open; will explode when ignited in close confinement; and will detonate if initiated by contact with a detonating primer of dry guncotton.

A small quantity of trinitrotoluene ignited in the open generally burns for a short time and then goes out; heat is dissipated by conduction, radiation, and the raising of the temperature of neighbouring particles of the explosive, until there is not sufficient heat available to raise the temperature of any remaining explosive to the ignition point. A larger quantity, once well ignited, will burn more and more fiercely and finally will often explode; heat is evolved more rapidly than it can be dissipated, raising the temperature of the explosive until it eventually explodes by reason of the energy imparted to it. If the breakdown of the molecular structure sets free more energy than is necessary for the breakdown of the contiguous molecules, an acceleration of the explosive process takes place and this continues until a certain maximum velocity is reached. This is called the velocity of detonation and is a constant for any one high explosive at a given density.

In general, velocities of detonation increase with an increase of density, but there is a limit beyond which further compression causes little or no change. The velocity of detonation of picric acid is about 5,980 metres per second at density 1·3 and 7,110 metres per second at density 1·5. Compression to density 1·6 only raises the velocity of detonation to 7,250 metres per second.

The characteristic of explosives used to initiate detonations, *e.g.* mercuric fulminate or lead azide, is a state of very unstable molecular equilibrium, which causes the above mentioned period of acceleration to be practically instantaneous.

The nature of the effects which are likely to be produced by an explosive may be predicted to some extent from its velocity of detonation. The greater this velocity, the greater will be the local effect of the detonation and the less will it be necessary to " tamp " the charge in order to get a satisfactory result.

The velocity of detonation may be measured by :

(*a*) The Mettegang recorder.
(*b*) Dautriche's method.
(*c*) Jones's condenser discharge method.

(*a*) *The Mettegang recorder.*

A diagrammatic representation of the instrument and electrical connections is given in Fig. 5.1.

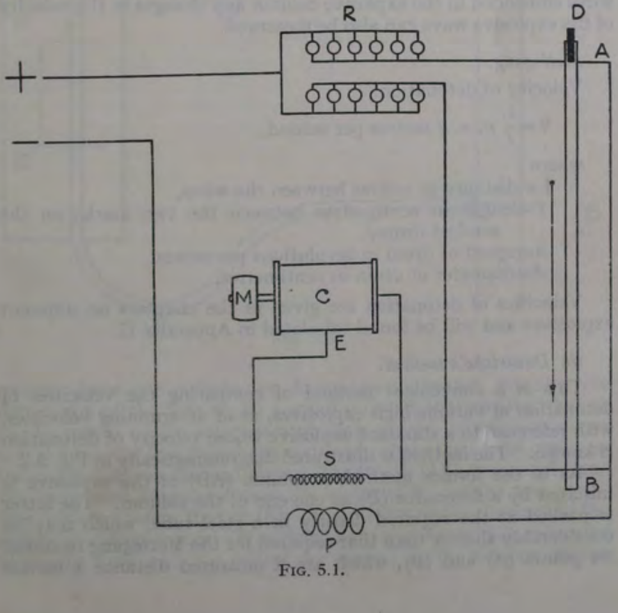


Fig. 5.1.

The explosive is packed at the required density in a long tube (AB), or arranged as a column of cartridges, and initiated by a detonator (D), at one end, so that an explosion wave passes down the column in the direction of the arrow. Two thin copper wires pass through the column at (A) and (B) a definite distance apart (of the order of 1 metre). These are ruptured as the explosion wave passes them. Each wire forms part of the circuit of the primary coil (P) of an induction coil and passes through a non-inductive high resistance (R), such as a bank of lamps. The rupture of each wire greatly alters the resistance, and so the current, in the primary circuit. This induces momentary high pressure currents in the secondary coil (S) of the induction coil, which is connected to a drum (C) and to a stylus of platinum (E) almost touching the drum. The drum is rotated at a known high speed by a motor (M). and the induced currents, making sparks between drum and stylus, mark the surface of the drum, which is smoked. The marking occurs at the rupture of each wire and the distance between the marks is measured microscopically. From this the time between the two sparks can be calculated, and hence the velocity of the detonation. This apparatus is capable of measuring periods of time of less than one millionth of a second. By using a series of wires embedded in the explosive column any changes in the velocity of the explosive wave can also be measured.

Mettegang.

Velocity of detonation.

$$V=\frac{L}{l}\,n.\,\pi.\,d \text{ metres per second,}$$

where

L=distance in metres between the wires,
l=length in centimetres between the two marks on the smoked drum,
n=speed of drum in revolutions per second,
d=diameter of drum in centimetres.

Velocities of detonation are given in the chapters on different explosives and will be found tabulated in Appendix II.

(*b*) *Dautriche's method.*

This is a convenient method of comparing the velocities of detonation of various high explosives, or of determining velocities, with reference to a standard explosive whose velocity of detonation is known. The method is illustrated diagrammatically in Fig. 5.2.

As in the former method, a column (AB) of the explosive is initiated by a detonator (D) at one end of the column. The latter is packed at the required density in a steel tube, which may be considerably shorter than that required for the Mettegang recorder. At points (A) and (B), which are a measured distance x metres apart, the ends of a length of detonating fuze are attached to two detonators which are let into the column of explosive. The centre of this loop is straightened out and firmly attached to a lead plate (L). The fuze consists of lead or tin piping, filled with a high explosive, such as trinitrotoluene, at a given density. This is the standard whose velocity of detonation must be known, in order to determine that of the explosive column. The explosion wave passing down the column, on firing the detonator, initiates the detonation of the fuze at (B) a small interval of time after that at (A) by means of the detonators at these points. Explosion waves travel down the fuze from both ends and, where they meet, make an indentation (E) on the lead plate. The length (AE), measured along the fuze, must be greater than the length (BE), for the fuze at (A) was initiated before that at (B). If y metres be the distance of the indentation from a point (F) midway between (A) and (B), measured along the fuze, and if v metres per second be the velocity of the

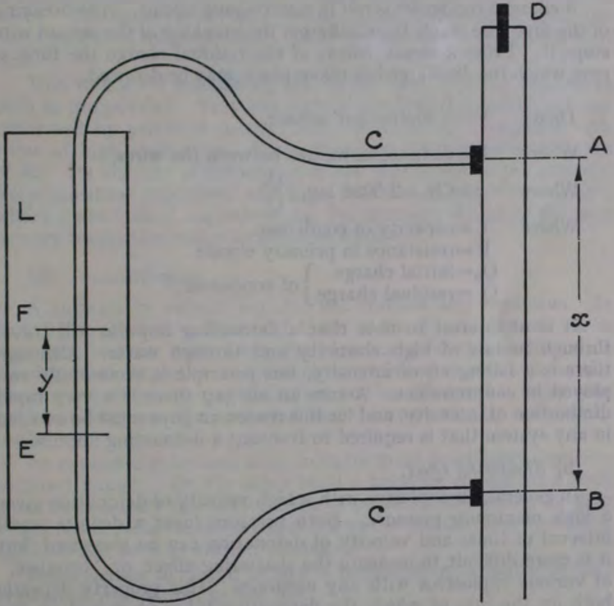


FIG. 5.2.

explosion wave in the detonating fuze, then V metres per second, the velocity of detonation of the material under test is given by :

$$V = \frac{v \times x}{2y.}$$

(c) *Jones's condenser discharge method.*

This depends on the fact that a really good electrical condenser will hold its charge for a long period.

A charged condenser is put in a Mettegang circuit. The breaking of the first wire starts the discharge, the breaking of the second wire stops it. From a measurement of the residual charge the time, *t*, over which the discharge has taken place, may be deduced.

Then $V = \frac{L}{t}$ metres per second,

Where L=distance in metres between the wires,

Where $t = CR. \times 2{\cdot}3036 \log_{10} \frac{Q_0}{Q'}$

Where C=capacity of condenser.
R=resistance in primary circuit

$$\left.\begin{array}{l} Q_0 = \text{initial charge} \\ Q = \text{residual charge} \end{array}\right\} \text{of condenser.}$$

It is of interest to note that a detonating impulse will travel through metals of high elasticity and through water. Although there is a falling off of intensity, this principle is successfully employed in countermines. Across an air gap there is a very rapid diminution of intensity, and for this reason air gaps must be avoided in any system that is required to transmit a detonating impulse.

(ii) *Shattering effect.*

In general, an explosive with a high velocity of detonation gives a high maximum pressure. Both pressure (over a definite small interval of time) and velocity of detonation can be measured, but it is more difficult to measure the shattering effect, or "brisance," of various explosives with any accuracy. This property depends both on the rate at which the detonation takes place and on the total energy content of the explosive. The mean maximum pressure is measured over a definite interval of time in the Hopkinson pressure bar test, and this may be taken as an indication of the comparative disruptive power of an explosive.

Useful information as to the efficiency of shell fillings can be obtained by detonating filled shell under water, or in sand, and examining the resulting fragmentation. This test gives results which are concordant with those obtained from the Hopkinson pressure bar.

Trauzl's test, which was standardized by the International Congress of Applied Chemistry at Berlin in 1903, has been largely used for the comparison of explosives, although it is a rough method and in many cases gives anomalous results. A cylindrical block of lead, 20 centimetres in diameter and 20 centimetres high, has a cylindrical hole 2·5 centimetres in diameter and 12·5 centimetres deep cast in it axially. Ten grams of the explosive under test are placed in the hole and " tamped " with dry sand. This charge is fired by an electric detonator, distending the cavity. The amount of this distension is taken as a comparative measure of the shattering effect. The figures given take 100 as an arbitrary standard for the effect produced by picric acid ; other explosives are compared with this.

This test gives misleading results for slow burning explosives such as gunpowder. Very low figures are obtained, which are not confirmed by practical results, weak as these are compared with those of high explosives. Mercuric fulminate only gives a figure of 42. Its velocity of detonation is low (3,000 metres per second). Very sensitive explosives are thus not necessarily very violent, whilst quite violent explosives, as, for instance, the amatols, may be very insensitive either to shock or friction.

(iii) *Insensitiveness*.

A sufficiently violent impulse will initiate any explosive. It may be applied as a frictional blow or by direct impact. It is necessary to have some comparative measure of the likelihood of ignition of an explosive in these circumstances, in order to fix the precautions necessary in manufacture and handling and to determine for what purposes the explosive may be conveniently and safely used.

An explosive to be used as an initiator must be suitably sensitive to direct impact. On the other hand a bursting charge for a shell must be decidedly insensitive both to impact and friction, so that it will not explode on the firing of the gun or on the shell striking a hard surface, such as armour plating.

Sensitiveness to direct impact is measured by a falling weight apparatus, represented in Fig. 5.3.

The figure of insensitiveness is a relative figure, that for picric acid being taken as standard at 100.

It is determined by allowing a weight to fall from varying heights on to samples of the explosive contained in caps inverted on an anvil in a gas-tight box which is connected to a calibrated manometer. The shock of the falling weight is transmitted to the explosive through a piston passing through a gas-tight joint in the cover of the box.

At each height of fall four caps of the explosives are tested alternately with four caps of picric acid and the total gas (if any) liberated noted as a percentage of the total which would have been liberated had complete explosion occurred.

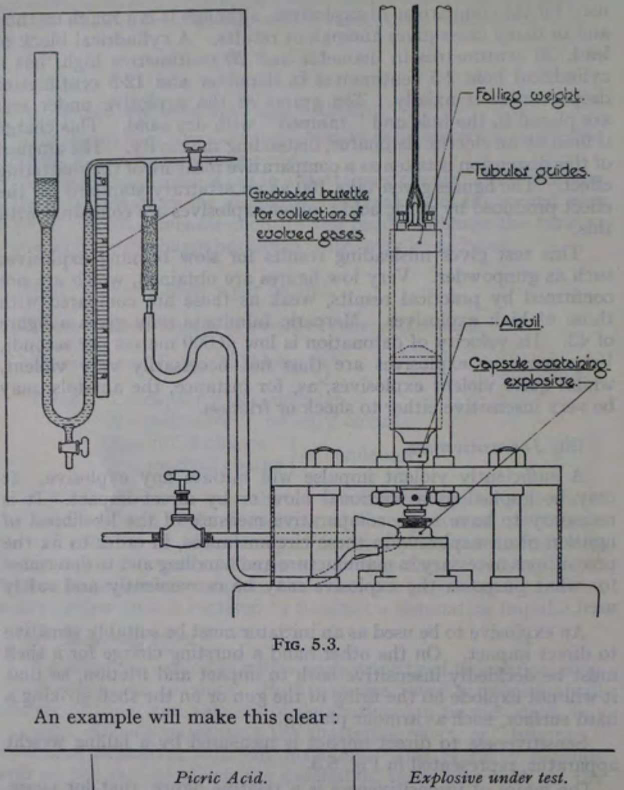


FIG. 5.3.

An example will make this clear :

Drop of weight in cms.	*Picric Acid.*		*Explosive under test.*	
	Total gas for 4 caps in c.c.	Percentage of total gas for 4 caps for complete explosion.	Total gas for 4 caps in c.c.	Percentage of total gas for 4 caps for complete explosion.
50	0	0	0	0
100	0	0	16	25
150	1	2	30	46
200	30	50	55	85
250	56	93	65	98
300	60	100	66	100

The percentage in each case is then plotted against the distances fallen by the weight :

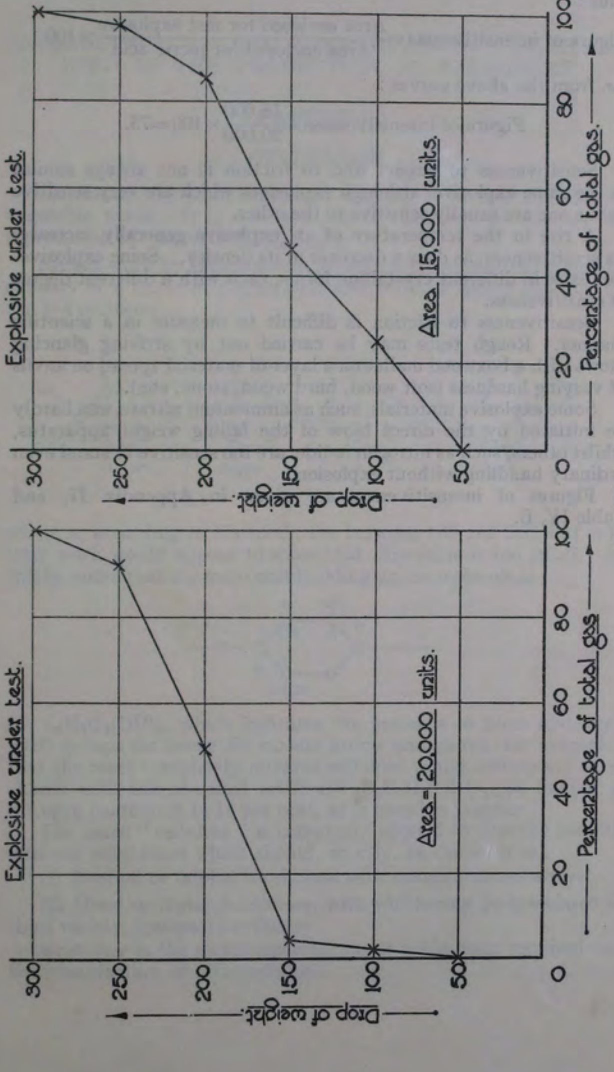


FIG. 5.4.

The areas enclosed by the two curves are then measured in any convenient units. The figure of insensitiveness is then calculated thus:

$$\text{Figure of insensitiveness} = \frac{\text{Area enclosed for test explosive}}{\text{Area enclosed for picric acid}} \times 100$$

i.e. from the above curves:

$$\text{Figure of insensitiveness} = \frac{15{,}000}{20{,}000} \times 100 = 75.$$

Sensitiveness to impact and to friction is not always similar in the same explosive, although explosives which are very sensitive to the one are usually sensitive to the other.

A rise in the temperature of an explosive generally increases its sensitiveness, as does a decrease in its density. Some explosives can exist in different crystalline forms, each with a different degree of sensitiveness.

Sensitiveness to friction is difficult to measure in a scientific manner. Rough tests may be carried out by striking glancing blows with a boxwood mallet on a layer of material spread on anvils of varying hardness (soft wood, hard wood, stone, etc.).

Some explosive materials, such as ammonium nitrate, can hardly be initiated by the direct blow of the falling weight apparatus, whilst others, such as nitrogen iodide, are too sensitive to stand even ordinary handling without explosion.

Figures of insensitiveness are given in Appendix II, and Table IV, B.

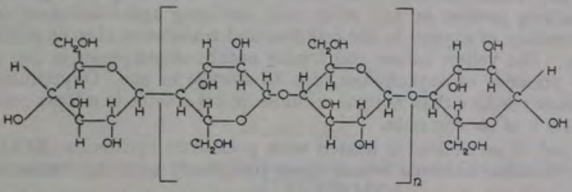
C.—MANUFACTURE AND PROPERTIES OF CHEMICALS USED IN THE PRODUCTION OF EXPLOSIVES

CHAPTER VI

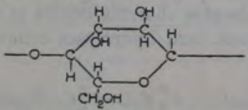
CELLULOSE

Cellulose is the main structural constituent of the cell walls of vegetable tissue. It is a very complex substance which may be represented by the formula $(C_6H_{10}O_5)^n$.

Recent work by Haworth and others indicates that the molecule consists of a chain of β-glucopyranose residues linked together in the 1–4 positions :



where *n*, according to Haworth, lies between 100 and 200, but still later work would appear to show that this value is too small. It will be noted that the main unit building up the molecule is



i.e. $C_6H_7O_2(OH)_3$, which indicates the presence of three hydroxyl (OH) groups for every six carbon atoms and shows, for example, that the most completely nitrated cellulose would correspond very closely with the so-called trinitrate $(C_6H_7O_2(ONO_2)_3)n$, having a nitrogen content of 14·14 per cent, as is found in practice.

The name " cellulose " is commonly applied to describe several different substances which should, strictly, be classified as :

(1) Normal or (alpha) α-cellulose with constitution as above.

(2) Hemi or (beta) β-cellulose, with which may be associated a third variety, (gamma) γ-cellulose.

α-cellulose is the most important, as it is the form required for the manufacture of nitro-cellulose.

Hemi or β-cellulose. This is distinguishable from the alpha variety by its higher chemical reactivity. It is reactive to weak reagents and is soluble in a 3 per cent. solution of caustic soda ($NaOH$). Hemi-cellulose usually forms unstable nitrates and is therefore undesirable for use in explosives manufacture. The above remarks apply to hydro- and oxy-cellulose (*see* below).

Normal or resistant cellulose. The following are a few of the distinctive reactions of normal cellulose.

(i) On treatment with dilute hydrochloric or sulphuric acid, α-cellulose changes to compounds of lower molecular weight, which contain higher percentages of oxygen and hydrogen. These are known as a whole by the name of hydrocellulose. This form of cellulose is more reactive than normal cellulose and is soluble in a 3 per cent. solution of caustic soda.

(ii) Normal cellulose is insoluble in a 3 per cent. solution of caustic soda.

(iii) Oxidation with dilute nitric acid, potassium permanganate, bleaching powder or any other mild oxidizing agent increases the percentage of oxygen in the cellulose and transforms it to oxycellulose. The yellow colour and friable nature of old paper is due to the presence of oxycellulose, due to storage in air. Oxycellulose is more reactive than normal cellulose and is soluble in a 3 per cent. solution of caustic soda.

(iv) If α-cellulose is heated with potassium hydroxide (KOH), the cellulose molecule breaks down completely with the formation of potassium oxalate $\left\{\begin{matrix}CO.OK \\ | \\ CO.OK\end{matrix}\right\}$ and water. In fact, oxalic acid is thus prepared in commerce from wood sawdust and caustic potash.

(v*a*) Concentrated sulphuric acid gives a sulphuric ester with α-cellulose, but considerable charring occurs at the same time.

(v*b*) Dilute sulphuric acid hydrolyses cellulose, a sugar, cellobiose, being formed :

$$(C_6H_{10}O_5)_n+\frac{n}{2}H_2O \rightarrow \frac{n}{2}\underset{\textit{Cellobiose.}}{C_{12}H_{22}O_{11}}$$

Action of nitric acid on cellulose.

The factors which determine the degree of nitration of the cellulose are the strength of the acid used and the temperature of and duration of nitration. Table 6.A. shows the service and commercial uses of various nitrocelluloses containing from 10·7 to 13·2 per cent. of nitrogen. The lower nitrated celluloses are much used in commerce for the manufacture of substances such as celluloid, artificial silk and leather, etc., owing to their ready solubility in many organic solvents.

As an example of the uses of nitrocellulose for purposes other than explosives *collodion* may be taken. This product consists of a soluble nitrocellulose dissolved in ether/alcohol, together with camphor and castor oil. This leaves a film which does not contract on drying. One of the most familiar applications of collodion is as a strengthening coating on incandescent gas mantles, to enable them to withstand transport and handling. Any contraction of the collodion on drying would destroy the gas mantle.

Cellulose nitrate was formerly of great importance in the manufacture of artificial silk by the Chardonnet process. This process has, however, been almost entirely replaced by the viscose process of Cross and Bevan and the cellulose acetate (Cellanese) process. α-cellulose is soluble in a few reagents. It is directly soluble in an ammoniacal solution of copper hydroxide (Schweizer's reagent) and also in a solution of zinc chloride in hydrochloric acid (Pauly's reagent). Its direct solubility in this way is, however, limited, but it can be readily dissolved by indirect methods.

Cellulose for the manufacture of nitrocellulose comes from three sources :

(*a*) Cotton.
(*b*) Wood.
(*c*) Annual plants.

TABLE 6.A.

COMPOSITION, PROPERTIES AND USES OF CELLULOSE NITRATES

Percentage Nitrogen.	USES.	
	Propellants.	Commerce.
10·7–11·2	—	Celluloid.
11·2–11·7	—	Photographic films. Artificial silk. Lacquers.
12·2	Cordites R.D.B., S.C.	Artificial leathers. Lacquers.
12·6	Ballistite N.C.T. N.C.Z.	—
13·1	Cordites Mk. I, M.D., M.C., and W.	—
13·2	N.C.Z.	—
14·14	Theoretical percentage for complete nitration to cellulose trinitrate.	

Notes :

(i) N.C. containing N = 11·1 per cent., often called the " dinitrate," as this corresponds with the formula $C_6H_7O_2OH(ONO_2)_2$.

(ii) N.C. containing N = 13·1 per cent., is called " guncotton ".

(iii) The stability of N/C DECREASES with increase in N content.

(iv) Solubility :—

- (*a*) All types are soluble in acetone.
- (*b*) As percentage N is increased, the solubility in other solvents decreases, thus :

  Up to 11·2 per cent. N—soluble in alcohol.
  Up to 12·5 per cent. N—soluble in ether/alcohol mixtures.
  Above 13·0 per cent. N—insoluble in ether/alcohol.

(*a*) *Cotton cellulose.* The seed of the cotton plant is surrounded by a light fibrous mass of almost pure cellulose. This material is collected, and, after cleaning and picking, forms the raw material of the cotton industry. The shorter strands are called linters. Cotton cellulose is a white, fibrous substance. Fig. 6.1. shows the twisted structure of a cellulose from cotton.

For explosive purposes cotton is used in the form of best cotton waste. This cotton must pass certain tests before acceptance. Of these tests the chief are as follows (W.D. Specification P. 279) :

(1) *Oil and grease.* These must *not* exceed 0·4 per cent. as determined by extraction with ether in a Soxhlet extractor.

(2) *Non a-cellulose.* These must *not* exceed 3 per cent. This is tested by extraction with a 3 per cent. solution of caustic soda.

(3) *Inorganic matter* (dust, grit, etc.). This must not exceed a total of 1·2 per cent. This is determined by ashing a sample of the cotton.

(4) *Woody fibre* (containing lignins and cuto-celluloses). This is detected by the Malachite Green dyeing test. A sample is dyed with Malachite Green and is then bleached with bleaching powder. Any woody fibre remains green. The amount must *not* exceed that in a sample which is kept by the W.D. Chemist at Woolwich.

(5) Moisture should not exceed 7·5 per cent. as determined by a drying test.

(6) When the cotton is dissolved in Schweitzer's reagent (cuprammonium hydroxide solution) under given conditions, the absolute viscosity of the resulting cotton solution must be 25 poises (metric units), as determined by Ostwald's falling steel ball method. This test has for its object an estimation of the comparative molecular size of the cellulose in the sample.

(*b*) *Wood cellulose.* The War Department lays down no stringent tests for this, as it is made under inspection. The moisture content must not, however, exceed 8 per cent.

When the Great War accentuated the need for indigenous sources of supply, attention was directed to the possibility of replacing cotton, as a source of cellulose, by wood.

[*To face page* 42.

Fig. 6.1.
Photomicrograph of Cotton Cellulose.
× 100.

Wood contains a large proportion of cellulose, but the nature and extent of the impurities present necessitate drastic methods of purification. To a certain extent the methods and machinery for producing wood cellulose lie ready to hand in the paper-making industry, although the majority of the wood pulp is imported. Our principal sources of supply are Norway, Sweden and Finland. These sources are close to Britain, but might be denied to us in time of war. In an emergency it might be possible to arrange for home production in its entirety.

The general scheme for the preparation of cellulose from wood is as follows :

(*a*) The wood is split into small pieces and is subjected in a high pressure boiler (autoclave) to the action of caustic soda and sodium sulphide (sulphate pulp process). The major portion of the impurities (lignin and cuto-cellulose) is thereby removed and the wood is reduced to a pulp. This pulp is thoroughly washed with water and strained.

(*b*) Colouring matter and certain other impurities are removed by the action of bleaching liquor, the process being accelerated by passing the pulp through a beater, in which it is subjected to the action of rapidly rotating knives. Cellulose which has to be nitrated must not be bleached too drastically or the fibres become disintegrated, thus causing serious detriment to subsequent nitration.

(*c*) After the excess of the bleaching liquor has been washed out, it is usual to add sodium sulphite (Na_2SO_3) or some other substance which will eliminate any residual chlorine retained from the bleaching liquor.

(*d*) All soluble salts are then removed from the pulp by thorough washing with water.

Wood cellulose is nitrated in the form of thin paper. Strict attention is paid to the uniformity of thickness and texture of the material. Absolute cleanliness is essential ; grease spots and metallic fragments render the cellulose useless for nitration. Before nitration the thin paper is either

(*a*) cut into small rectangles ; or

(*b*) corrugated and made into a roll with plain paper ; a layer of corrugated paper being put on top of a layer of plain paper and the two rolled up together. This gives the advantage of a compact roll which, however, presents a maximum possible surface to the nitrating acid.

Whether cellulose in the form of cotton or paper from wood is nitrated, the methods of nitration and of subsequent treatment of the nitrated product do not differ widely in principle.

(*c*) *Cellulose from annuals.* Recent work has shown that a satisfactory cellulose can be made from straw, and research is also being undertaken to investigate the production of cellulose from other materials, such as esparto grass.

General. Cellulose from any source contains the following impurities in a greater or less degree and they must be removed before nitration can be attempted.

1. *Extraneous matter picked up during manufacture.*

(*a*) *Oil or grease.* This is removed by treatment with a suitable solvent such as trichlorethylene or benzene.

(*b*) *Particles of dust, grit and metal.* Sifting will remove most of this, while particles of iron or steel can be removed with the aid of magnets.

(*c*) *String, wood, etc.* These are picked out by hand.

2. *Non α-cellulose.*

Boiling with a 3 per cent. solution of caustic soda will dissolve out these substances. Further purification is achieved by bleaching the cotton with bleaching powder or sodium hypochlorite, the bleach to contain not more than 0·5 part and not less than 0·3 part of available chlorine to 100 parts of cotton waste.

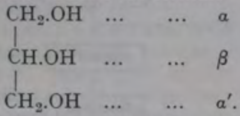
The supply and purification of cellulose for the purpose of nitration is governed by the W.D. Specification P. 279 (to govern manufacture and inspection of nitrocellulose for land and air services).

CHAPTER VII

GLYCERINE

Glycerine is the raw material for the manufacture of trinitroglycerine and dinitroglycerine.

Glycerine is a trihydric alcohol and is known to chemists as glycerol, the suffix -ol being used to denote an alcohol. Chemically it is trihydroxy propane, and has the formula



$$\begin{array}{lccl} CH_2.OH & \ldots & \ldots & \alpha \\ | & & & \\ CH.OH & \ldots & \ldots & \beta \\ | & & & \\ CH_2.OH & \ldots & \ldots & \alpha'. \end{array}$$

Occurrence. Glycerine is not found in nature as such, but in the form of its esters with various organic acids. Those esters which are solid at the ordinary temperature are called fats; those which are liquid are called oils. The fats contain such acids as butyric, palmitic and stearic, while the oils contain chiefly unsaturated acids such as oleic.

Preparation. Glycerine is obtained from fats by splitting the fat into the glycerine and fatty acid from which it was derived. The general reaction involved is:

Fat+water → Glycerine+fatty acids.

A summary of the four principal methods of obtaining glycerine from fat is shown on the Flow Diagram (Fig. 7.1.).

1. *Soap boiling process.* The fat is boiled with water and caustic soda in a vat. The following reaction occurs:

Fat+caustic Soda → Glycerine+soap.
(Sodium salt of fatty acid).

In order to separate the soap, salt is added to the vat, when soap settles out on the top, and is skimmed off. The "sweet water," which is run off at the bottom of the vat, contains glycerine, salt, sodium carbonate, etc.

2. *Autoclave process.* This takes place at 220° C. and under 20 atmospheres pressure. (300 lb./in.^{2}.) At the end of three hours' boiling the fatty acids and their calcium salts settle out at the top. The liquor which contains the glycerine is sent to the vacuum pan.

3. *Twitchell process.* The twitchell reagent is a black liquid which is obtained by dissolving naphthalene in oleic acid and then adding sulphuric acid. The process is carried out in an autoclave at 100° C.

4. *Fermentation vat.* Ground castor seed contains lipase. Lipase is a ferment or enzyme, which also occurs in the digestive tracts of animals and has the power of splitting fats into glycerine and fatty acids. It works best in a slightly alkaline medium.

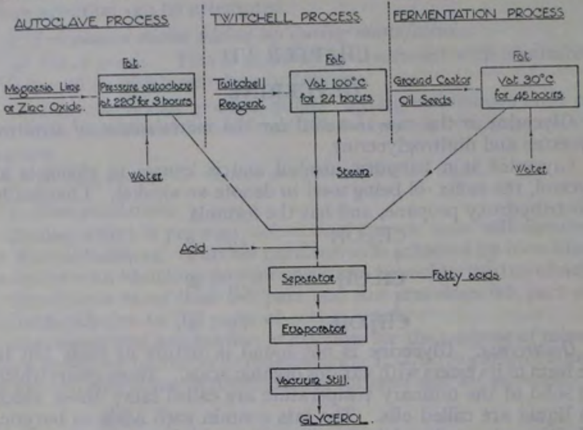


FIG. 7.1.

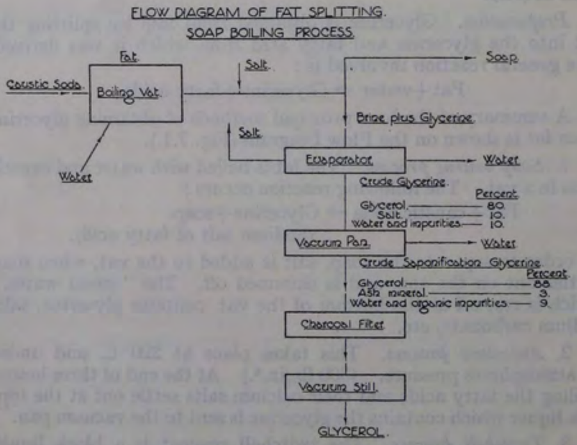


FIG. 7.1.

The glycerine resulting from this process has a slight castor oil flavour.

Nos. 3 and 4 above are used on the Continent, but are at present of little importance in England.

Purification of the glycerine.

Only glycerine from the soap boiling process is used for the purpose of nitration at the present time.

The *evaporator* gives a crude glycerine which contains 80 per cent. of glycerol, 10 per cent. of salt and 10 per cent. of water and impurities.

The *vacuum pan* continues the evaporation under reduced pressure and yields a brown and viscous product. This product contains 88 per cent. of glycerol.

The *vacuum still* is used for distillation of the crude glycerine under reduced pressure. The still has two " effects ", the steam from the first " effect " being used to give further distillation from the second " effect ". The yield from the vacuum still is yellow-green in colour and contains 98 per cent. of glycerol, together with water and colouring matter, and is known as " dynamite " glycerine. This is sufficiently pure for the purpose of being nitrated. Salt collects in salt boxes at the bottom of the vacuum stills and is drawn off periodically.

In order to obtain water-white anhydrous glycerine for medicinal purposes, " dynamite glycerine " is decolorized by passing it through animal charcoal and is then redistilled in vacuo.

Fermentation glycerine.

By suitably altering the conditions which are used in the production of alcohol from sugar by fermentation, it is possible to increase the yield of glycerine from under 2 up to 20 per cent. at the expense of the alcohol. This is done principally by employing special cultures of yeast in the presence of sodium sulphite. In this way it is possible to get from 100 parts of sugar by weight, approximately 20 parts of glycerol and 27 of ethyl alcohol. The process is chiefly used in Germany and the U.S.A. and might, in case of emergency, be used in this country.

Properties of glycerine. Pure anhydrous glycerol is a colorous viscous liquid with a sweet and slightly burning taste. It freezes at 20° C., but its F.P. is greatly depressed by the presence of small quantities of water which, owing to the hygroscopic nature of glycerine, are generally present in the liquid.

Glycerine boils at 290° C. with decomposition, but can be distilled under reduced pressure.

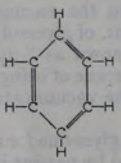
Glycerine for W.D. use must be free from salts and metals, sugar, molasses, fatty acids or other impurities. It must be transparent, " water white " in colour, odourless and free from acidity and suspended solid matter. Ash must not exceed 0·1 per cent.

Specific gravity must not be less than 1·26 at 60° F.

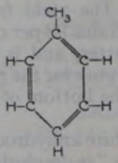
CHAPTER VIII

AROMATIC COMPOUNDS. BENZENE. TOLUENE. PHENOL. ANILINE

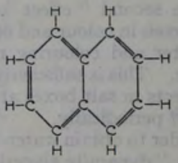
The aromatic compounds received their name originally owing to their aromatic odour. The term " aromatic " is now restricted to homocyclic compounds, which contain one or more six-membered carbon rings in their structure. Examples are :



Benzene C_6H_6.



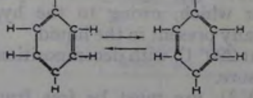
Toluene C_7H_8.



Naphthalene $C_{10}H_8$.

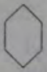
Structure of benzene.

The exact arrangement of the carbon and hydrogen atoms in the benzene molecule has for long been a matter of conjecture. Kekulé's formula, in which the carbon atoms each carry a hydrogen atom and are united to each other by alternate double and single bonds, is satisfactory in some respects but fails in others, in particular that benzene does not behave like an unsaturated compound and that the 1–2 and 1–6 positions (*see* later) are actually identical. Kekulé recognized this latter difficulty and suggested in explanation that the bonds oscillated thus :



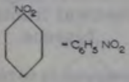
The modern view is that the structure is one of " resonance " or " mesomerism " between these two possible structures, the bonds between neighbouring carbon atoms being similar and intermediate between single and double ones. It also seems from spectral evidence that the plane, regular hexagonal model is correct.

Partly on account of not knowing the exact structure and partly to save time in writing, it is the custom to write benzene as a regular hexagon :



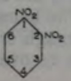
it being understood that there are carbon and hydrogen atoms at each corner, and this method is adopted throughout this book.

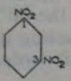
If one or more of the hydrogen atoms are replaced by other groups, then the group is written in the model, thus mononitrobenzene (M.N.B.) is shown as

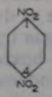


Nomenclature of the benzene derivatives.

It has long been known that the six positions in the benzene ring are identical, so that only one mono-derivative (for any one particular substituent) exists. When, however, a second substituent is introduced to form di-derivatives, three isomers may be produced. This may be clearly seen by taking as an example the substitution of the nitro-group into benzene. When nitric acid (in the presence of sulphuric acid) acts on benzene at comparatively low temperatures, mono-nitro-benzene ($C_6H_5NO_2$) is produced, and this on further nitration at higher temperatures is converted into di-nitro-benzene ($C_6H_4(NO_2)_2$), which exists in three isomeric forms (of widely differing melting points) having the formulæ :

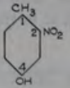




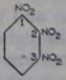


M.P. 118° C. 90° C. 172° C.
Name. 1.2. or ortho- 1.3 or meta- 1.4 or para-dinitrobenzene.
(Greek. Orthos=straight ; Meta=between ; Para=opposite).

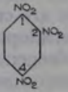
It is preferable to denote the position of the substituent group by numbering it the same as that of the carbon atom to which it is attached, the carbon atoms being numbered 1 to 6 in clockwise order. Hence the names become 1.2. dinitrobenzene, 1.3. dinitrobenzene and 1.4. dinitrobenzene, as shown above. This use of numbers is of greater importance when the substituent groups are different, *e.g.* ortho-nitro para-cresol having the formula



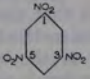
is better designated as 1. methyl. 2. nitro. 4. hydroxy benzene. The tri-derivatives are named thus :



1.2.3. or adjacent trinitrobenzene.



1.2.4. or unsymmetrical trinitrobenzene.



1.3.5. or symmetrical trinitrobenzene.

Importance of aromatic compounds in the manufacture of explosives.

Many aromatic compounds, when nitrated, give a group of very powerful high explosives.

Thus toluene gives tri-nitro-toluene (trotyl or T.N.T.), phenol gives trinitrophenol (picric acid) and aniline gives (via dimethyl aniline) the very sensitive symm. trinitrophenyl methyl nitramine (tetryl or composition exploding). m. dinitrobenzene is less powerful than the first three and is used in mining explosives such as bellite.

Occurrence of benzene, toluene and phenol.

When coal is distilled in absence of air, the resulting products are : (*a*) coal gas, (*b*) ammoniacal liquor, (*c*) coal tar, (*d*) coke. Coal-tar contains, inter alia, benzene, toluene and phenol. The coal gas is also rich in benzene and toluene, in fact the gas from one ton of coal contains, on the average, about 15 times as much benzene and toluene as does the tar. The benzene and toluene are extracted from the gas by passing it through creosote, the creosote being subsequently heated in order to recover the benzene and toluene which are condensed.

Toluene and some benzene are present in Borneo petroleum, in fact this was the source of much toluene for nitration to T.N.T., which benzene-toluene mixture is known as " Toluene-petrol ".

Syntheses of benzene and its homologues by passing acetylene through a red-hot tube :

$$\underset{\textit{Acetylene}}{3C_2H_2} \rightarrow \underset{\textit{Benzene}}{C_6H_6}$$

are of interest but are not of commercial importance in this country owing to the readiness with which benzene and toluene may be obtained from coal tar.

Benzene and its related aromatics may be obtained from coal tar (*a*) by the Lennard continuous process, or (*b*) by discontinuous distillation from a pot still.

The following is a description of the Lennard process, which is given as an example of the extraction of aromatics from tar.

The tar always contains a certain amount of moisture, and this is evaporated off by letting the tar act as a cooling agent in the condensers (Fig. 8.1.). The resulting anhydrous tar is then vaporized in the gas-heated vaporizing coils and the vapour is condensed in a series of condensers, the higher-boiling fractions being condensed first. The fractions obtained are :

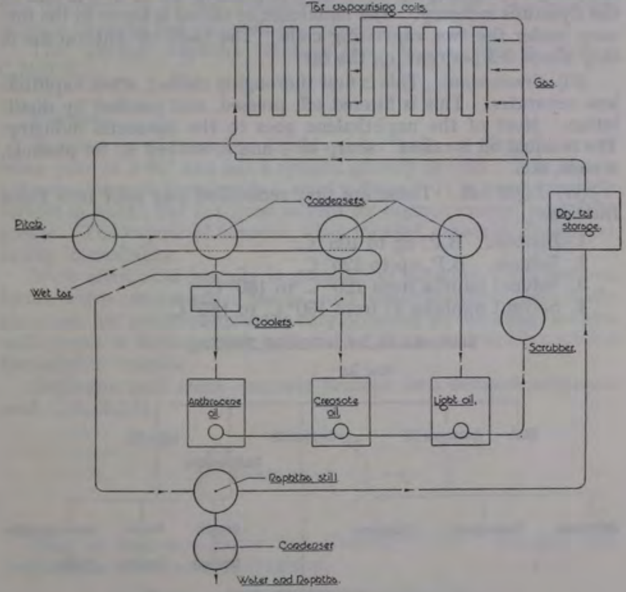


FIG. 8.1.

(i) *Pitch.* This goes to the pitch bays, where it sets to a viscous mass which has the appearance of a solid. This can be broken with a hammer, and shows a conchoidal fracture. A heap of pitch, however, will flow out into a pool in the course of months.

(ii) *Anthracene oil.*

(iii) *Creosote oil.*

(iv) *Light oil.*

In addition there is "*Best naphtha*" which is obtained from the naphtha still (Fig. 8.1.).

Working up of the fractions from the Lennard process.

(i) *Pitch.* This is sold for briquetting.

(ii) *Anthracene oil.* This is first cooled, when crude anthracene separates. This is separated from the rest of the oil by means of a centrifuge. The impure anthracene is green in colour and is sold to the dyestuffs industry. The remainder of the oil is burnt in the furnace under the two vaporizing coils. The yield of anthracene is only about 0·3 per cent. on the tar.

(iii) *Creosote oil.* This is first thoroughly chilled, when naphthalene separates. This is filtered off, pressed, and purified by distillation. Most of the naphthalene goes to the dyestuffs industry. The residual oil is called "sharp oil" and is worked up for phenols, cresols, etc.

(iv) *Light oils.* These are first redistilled and split into three fractions :

1. Benzole. B.P. up to 105° C.
2. Toluole. B.P. up to 120° C.
3. Solvent naptha from 120° C. to 160° C.
4. Solvent naphtha II from 160° C. to 180° C.

SUMMARY OF THE LENNARD PROCESS.

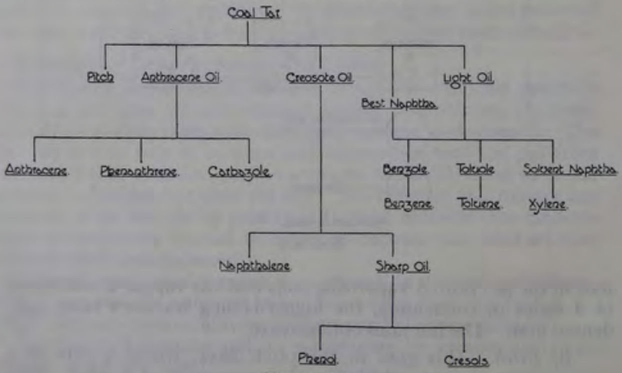


TABLE 8.A.

The benzole fraction is first washed with dilute sulphuric acid to remove the basic substance pyridine C_5H_5N as sulphate. Then comes a wash with concentrated sulphuric acid to remove "unsaturated" hydrocarbons and sulphur compounds such as thiophene, C_4H_4S. A further wash with water removes sulphuric acid. The liquid is finally washed with caustic soda and is redistilled by means of an elaborate column. Carbon disulphide, CS_2, passes over first, the receiver is changed and benzene passes over at 80° C. When most of the benzene has passed over, the toluol fraction, which has also been worked, is added to the still. More benzene is obtained, the receiver is changed again and a mixture of benzene and toluene comes over and is added to the next batch. When the temperature of the distillate has reached 110°, the receiver is again changed and pure toluene comes over.

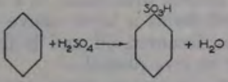
The solvent naphtha fraction gives o., m. and p. xylene $C_6H_4(CH_3)_2$.

Benzene.

Benzene is a colourless liquid which boils at 80·2° C., melts when pure at 5·49° and has a specific gravity of 0·88. It is highly inflammable and burns with a smoky flame. It is very sparingly soluble in water, but is a good solvent for organic matter, especially grease. The vapour of benzene, when inhaled, causes giddiness and finally insensibility.

With nitric acid (usually in presence of sulphuric acid) benzene forms nitro-compounds. Mono- and dinitrobenzene are easily obtained, but trinitrobenzene is only obtained by nitrating benzene with excess of fuming nitric acid and sulphuric acid which contains free sulphur trioxide.

Sulphuric acid alone converts benzene into benzene sulphonic acid, $C_6H_5.SO_3H$.



Uses of benzene.—Motor fuel (Benzol), "dry" cleaning and preparation of benzene derivatives.

Toluene (Methyl-benzene. $C_6H_5.CH_3$)

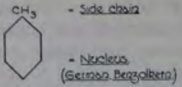
Preparation.

1. From coal-tar light oils.

2. Borneo petroleum also contains toluene. It is impossible to isolate this toluene, but a fraction can be obtained containing about 50 per cent. of toluene. This can be used for the preparation of derivatives such as trinitrotoluene.

Properties. Toluene is a colourless liquid which boils at 111° C. and can only be frozen by cooling to —95° C. Like benzene it burns with a luminous smoky flame. The vapour of toluene, like that of benzene, is slightly toxic.

Toluene differs from benzene in that, besides the nucleus or benzene ring, it contains a *side-chain* (the methyl group). Thus :



The nucleus will undergo the normal reactions of benzene. It may be sulphonated or nitrated. (In fact trinitrotoluene is much easier to prepare than trinitrobenzene).

The side-chain or methyl group is capable of undergoing separate reactions. Thus, by the action of potassium permanganate, it may be converted into the carboxylic acid group COOH, and we obtain benzoic acid. The permanganate supplies the necessary oxygen.

$$\underset{\textit{Toluene.}}{C_6H_5.CH_3} \xrightarrow{_3O} \underset{\textit{Benzoic acid.}}{C_6H_5CO.OH}+H_2O.$$

Phenol (hydroxy-benzene, carbolic acid, phenic acid, C_6H_5OH).

Preparation.

1. From coal tar. (*See* above.)

2. From benzene sulphonic acid by fusion with caustic soda. Phenol was thus made, during the Great War, following a process developed at Sutton Oak. Since the supply of coal-tar phenol might be insufficient in an emergency, the Sutton Oak process might have to be readopted. A summary of the process is given in Fig. 8.2.

The fused mass is treated with water, in a dissolver when sodium phenate dissolves, and forms a layer above the sodium sulphite. This aqueous layer is decanted off and is treated with sulphuric acid in a decomposer to give phenol.

$$2C_6H_5.ON_a+H_2SO_4 \rightarrow \underset{\textit{Phenol}}{2C_6H_5OH}+\underset{\text{Sodium Sulphate.}}{Na_2SO_4}$$

The phenol is then purified by distillation from a STILL.

The overall yield from the process is 60 per cent. of the theoretical yield.

Properties of phenol. Phenol forms colourless crystals which melt at 41° C., when pure, and boil at 183° C. Phenol is sparingly soluble in water and at the same time water is slightly soluble in phenol, whose M.P. is greatly depressed by the presence of small quantities of water. Owing to this fact, and to the readiness with which phenol takes up moisture from the air, a stock of phenol is apt to go liquid unless kept in carefully sealed containers. When exposed to air and light, phenol readily turns pink. Phenol has the well-known " disinfectant " carbolic acid smell and is unsuitable for internal use owing to its toxic nature. Owing to the presence of the acidogenic benzene nucleus, phenol shows acid properties.

It is, however, a very weak acid, phenol being liberated from its salts (phenates) even by such weak acids as carbon dioxide. Thus:

$$2C_6H_5ON_a + H_2O + CO_2 \rightarrow 2C_6H_5OH + Na_2CO_3.$$

Sodium phenate. Sodium carbonate.

The addition of nitro groups to the nucleus greatly increases the acidic nature of the hydroxyl group. Thus picric acid (s. trinitrophenol) is a relatively strong acid and readily forms salts with metals, some of these salts being very sensitive to shock and friction (*see* later under picric acid)

MANUFACTURE OF PHENOL BY THE SUTTON OAK PROCESS.

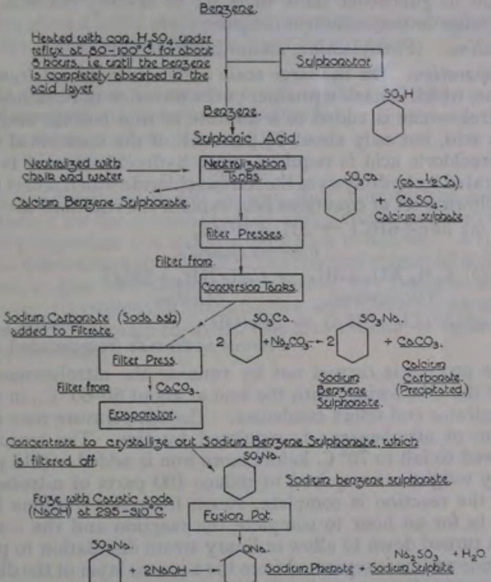
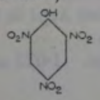


FIG. 8.2.



Picric Acid.

Phenol may readily be sulphonated or nitrated.

Uses of phenol.

(1) In the service, for the manufacture of picric acid (*q.v.*)

(2) In the drug industry, for the manufacture of aspirin, salol, betol, etc.
(3) In the dyestuff industry.
(4) For the manufacture of phenol formaldehyde resin (Bakelite).
(5) Still, to a certain extent, as a disinfectant.

Sodium phenate. ($C_6H_5.ON_a$) is used in the service for incorporation in guncotton slabs in order to destroy bacteria, which might cause decomposition of the guncotton.

Aniline. (Phenylamine, amino-benzene, $C_6H_5.NH_2$).

Preparation. On the large scale aniline is prepared from nitrobenzene, which is itself a product of the nitration of benzene.

Nitrobenzene is added to a mixture of iron borings and hydrochloric acid, but only about 2½ per cent. of the theoretical amount of hydrochloric acid is required, since hydrochloric acid is largely regenerated by hydrolysis of the ferrous chloride which is first formed. The following set of equations best explain the reactions involved :

(*a*) $3Fe+6HCl \rightarrow 3H_2+3FeCl_2$
Ferrous chloride.

(*b*) $C_6H_5.NO_2+3H_2 \rightarrow C_6H_5.NH_2+2H_2O.$
Nitrobenzene. *Aniline.*

(*c*) $3FeCl_2+6H_2O \rightarrow 3Fe(OH)_2 \quad +6HCl.$
Ferrous hydroxide (regenerated acid).

The process is carried out by running the nitrobenzene on to part of the iron borings with the acid at about 50–60° C., in a vessel with agitator and reflux condenser. The temperature rises and the addition of nitrobenzene is regulated by this. The temperature is allowed to fall to 70° C. before more iron is added. (115 parts of iron by weight are required to reduce 100 parts of nitrobenzene.) When the reaction is complete, steam from the " aniline boiler " is run in for an hour to complete the reaction and the condenser is then turned down to allow ordinary steam distillation to proceed. The crude aniline is separated from the aqueous layer of the distillate. This aqueous layer contains 3 per cent. of aniline and is returned to the aniline boiler to present loss of aniline. The crude aniline. is rectified by distillation in vacuo. The first runnings contain a little benzene, water and aniline. The yield of pure aniline is about 90 to 95 per cent. of the theoretical yield.

Properties of aniline. Aniline is colourless if pure, but turns yellow and finally brown when kept in the light. It may always be decolorized by redistillation.

B.Pt. 184° C. Sp. gr. 1·023 at 15° C. Solubility 1 part aniline in 31 of water.

Aniline is rather poisonous and is readily absorbed by the skin.

From the chemical point of view aniline is ammonia in which one of the hydrogen atoms has been replaced by the phenyl group

(C_6H_5). Owing to the acidogenic nature of the phenyl group aniline is a much weaker base than ammonia.

Aniline forms salts with acids, but these are readily decomposed by other bases, even by ammonia :

$$\underset{\text{(anilinium chloride).}}{\underset{\text{Aniline hydrochloride}}{C_6H_5.NH_3Cl}}+NH_3 \rightarrow \underset{\text{chloride.}}{\underset{\text{ammonium}}{NH_4Cl}}+C_6H_5.NH_2$$

Aniline gives a brilliant but evanescent purple colour with bleaching powder. This is a very delicate test for aniline.

Uses.

(1) In the service, for making tetryl (*q.v.*).
(2) Extensively in the dyestuff industry.
(3) For drugs, such as phenacetin.

Summary.

From the foregoing it will be seen that many of the essential raw materials for the manufacture of high explosives are also used in the very important dye and synthetic drug industries. A country which has a flourishing dye industry has the best chance of obtaining explosives in case of emergency, as existing dye factories may be turned over to explosives manufacture and there exists a large technical staff of organic chemists, who may quickly be turned over to explosives work.

CHAPTER IX

FIXATION OF NITROGEN. AMMONIUM NITRATE. SALTPETRE

Nearly all explosive substances contain nitrogen. In the manufacture of explosives, nitrogen is generally needed in the form of nitric acid (HNO_3), but other nitrogen compounds which are in great demand for the same purpose are ammonium nitrate (NH_4NO_3), which is used in the amatols and ammonals, barium nitrate, $Ba\ (NO_3)_2$, and saltpetre (potassium nitrate (KNO_3), which is the principal constituent of gunpowder.

Sources of nitrogen.

1. *Saltpetre.*

By the action of various bacteria, decaying animal and vegetable matter gives rise to small quantities of nitric and nitrous acids, which, by inter-action with potash salts in the soil, give rise to saltpetre or potassium nitrate.

In the hot climate of India, much saltpetre is produced in this way and thousands of tons of crude saltpetre are thus obtained every year and are shipped to Europe.

In France, the need of saltpetre for gunpowder manufacture led to the raising of special commissioners called Salpétriers, whose duty it was to collect saltpetre from cellars, old walls, etc. In good years as much as 3,000,000 pounds of saltpetre were produced in France in this way.

Saltpetre was also obtained from artificial nitre beds, consisting of earth mixed with animal and vegetable matter, ashes, lime and marl. The mixture was heaped up with twigs, and intersected by holes to allow free access of air. It was turned periodically and moistened with urine. The nitrate, which gradually formed in the mass, was extracted with water. Saltpetre is now almost entirely made by the conversion process (*see* below under " Saltpetre ").

2. *Chile saltpetre* (Nitre, Sodium nitrate $NaNO_3$).

This salt occurs as a widespread deposit in the desert lands of Chile, Peru and Bolivia, where it is found mixed with soil and covered with layers of clay containing gypsum. The nitre beds have a width of two miles, a thickness of three to 15 feet, and stretch over a distance of 150 miles. The crude caliche extracted from them contains up to 65 per cent. of sodium nitrate, together with potassium nitrate (2 to 15 per cent.) ; sodium chloride (up to 20 per cent.) ;

sodium iodate, chlorate and perchlorate; and gypsum. After being refined by recrystallization from boiling water, the product contains 95 per cent. of sodium nitrate, with about 1 to 2 per cent. of sodium chloride and smaller quantities of sodium sulphate and perchlorate.

3. *Ammonia* (NH_3) from gasworks.

In peace time, this is usually converted to ammonium sulphate, $(NH_4)_2SO_4$, and sold as a fertilizer, but in a war it could, if required, be converted into ammonium nitrate.

4. *The atmosphere.*

Normal air contains 78 per cent. of nitrogen by volume or 75½ per cent. by weight. It has only been possible since the beginning of this century for man to draw on this atmospheric nitrogen.

Fixation of nitrogen

In view of the fact that nitrogen is constantly being lost to the air, as elementary nitrogen, whenever a nitrogenous body undergoes decomposition, and owing to the increasing use of combined (fixed) nitrogen as a fertilizer and in the dyestuffs and explosives industries, the need for some process whereby the nitrogen of the air could be utilized began to be pressing as early as 1890. Lord Kelvin predicted that, at the then prevailing rate of using nitrates, the supplies of Chile saltpetre would soon become exhausted and that, owing to lack of fertilizer, there would ensue a world famine. Lord Kelvin's prediction acted as a stimulus to research and, very soon, various processes for fixing atmospheric nitrogen were evolved.

That strange genius, Henry Cavendish, had discovered so long ago as 1780 that, when electric sparks are passed through air and the resulting gases dissolved in water, nitric acid is formed. This action occurs in nature to some extent, rain water having been shown to contain traces of ~~nitrogen~~ NITRIC ACID after a thunderstorm. am 1

Cavendish's discovery formed the basis of the Birkeland-Eyde process, which was formerly used in Norway. In this process oxides of nitrogen were formed by passing air through a high tension arc and were dissolved in water to give nitrous and nitric acids. Some of the nitric acid was concentrated and the rest was converted into calcium nitrate $Ca(NO_3)_2$ by the action of chalk and was sold as Norway saltpetre.

Present processes for the fixation of nitrogen

Imperial Chemical Industries plant at Billingham.

The plant started work in 1921 and fixed two tons of atmospheric nitrogen a day. It now fixes about 600 tons a day.

There are two distinct processes; first the conversion of nitrogen to ammonia by the Haber-Bosch process, and secondly the conversion of ammonia to nitric acid by the Ostwald process.

(*a*) *Haber-Bosch process.* The essential reaction involved is :

N_2	+	$3H_2$	$\rightleftarrows$	$2NH_3$
Nitrogen		Hydrogen	(reversible reaction)	Ammonia
1 volume		3 volumes		2 volumes.

The necessary mixture of one part of nitrogen to three of hydrogen by volume is obtained from water gas and producer gas.

These show the following average analyses :

Constituent.	*Water gas per cent.*	*Producer gas per cent.*
Carbon dioxide CO_2	5	5
Carbon monoxide CO	45	25
Hydrogen H_2	50	5
Nitrogen N_2	Nil	65
	100	100

These two gaseous mixtures are blended in such proportions as to give a mixture which contains 75 of hydrogen to 25 of nitrogen by volume.

To the resulting mixture superheated steam is added and the whole is passed over a catalyst (*i.e.* a substance which assists the progress of the reaction without itself undergoing permanent chemical change). The catalyst used here is a porous form of iron, which is mixed with alumina (Al_2O_3) and moistened with caustic potash solution.

On passage over the catalyst, the following reaction occurs :

$$\mathrm{CO+H_2O} \underset{\substack{\text{in presence of}\\ \text{iron catalyst.}}}{\rightarrow} \mathrm{CO_2+H_2+9{\cdot}96K.}$$

The exit gases (CO_2=30, CO=3, H_2=52, N_2=15 per cent.) are compressed to 50 ats (1 " at "=14·7 lb. per square inch) and the carbon dioxide is washed out by water, the resulting high pressure solution being used to generate power. The residual gases are then compressed to 250 ats. If so desired, a proportion of the gas can then be passed over a catalytic mixture of zinc chromate and copper powder at 400° C., whereby methyl alcohol (CH_3OH) is formed, and is removed from the residual gas.

$$\mathrm{CO+2H_2} \underset{\substack{\text{catalyst at}\\ 400^\circ\text{ C.}}}{\rightarrow} \underset{\text{Methanol}}{\mathrm{CH_3OH}}\mathrm{+27{\cdot}2K}$$

The balance of the carbon monoxide is removed by " copper liquor " (copper tetrammine formate) at 200 to 250 ats, whereby the carbon monoxide forms an addition compound with the copper liquor and the carbon monoxide content of the gases is reduced to three parts to the million.

The residual gases (hydrogen, 75 per cent. ; nitrogen 25 per cent.) now go to the "converter columns". These are steel towers, which are closed at the top by a large screwed plug. Each column is 5 feet in diameter and about 25 feet high. The size of column and quantity of iron-alumina-potash catalyst are so designed as to give the optimum time of passage of the gases over the catalyst. 12 per cent. of the gases are thereby converted to ammonia, which is now washed out with water in absorbtion towers on the "counter current" system, water being made to trickle *down* the tower and the gases being passed *up* the tower. The resulting solution of ammonia passes out at the bottom of the tower. The unconverted hydrogen-nitrogen mixture passes out at the top of the tower, is reinforced with more of the same mixture from the "copper liquor" towers and is passed again through the converter columns. The various reactions which occur during the stages of purification and conversion are exothermic and supply sufficient heat to make the process thermally self-supporting.

(*b*) *Conversion of ammonia to nitric acid by the Ostwald process.*

A mixture of ammonia with excess of air is preheated to 150° C. and is then passed over a platinum gauze catalyst, whereby nitric oxide is formed :

$$4NH_3+5O_2 \rightarrow 4NO+6H_2O \text{ (steam)}+214{\cdot}2K.$$

Part of the heat evolved keeps the platinum catalyst red hot. The remainder of the heat is absorbed by cooling water.

The gases pass through a filter which is filled with granite chippings, and through a heat recuperation system. Then the gas is cooled, whereby nitrogen peroxide is formed :

$$2NO+O_{2\ \text{(air)}} \rightarrow 2NO_2+35{\cdot}2K.$$

On absorbing the gases in water, nitric acid is formed :

$$4NO_2+O_2+2H_2O \rightarrow 4HNO_3.$$

Some of this nitric acid is neutralized by soda ash (Na_2CO_3), thus giving sodium nitrate :

$$Na_2CO_3+2HNO_3 \rightarrow 2NaNO_3+H_2O+CO_2.$$

This is the source of the sodium nitrate which is now used by the Royal Naval Cordite Factory, Holton Heath, for re-conversion to nitric acid. At first sight it would appear to be redundant to convert this acid to the sodium salt and then reconvert it to nitric acid at the cordite factory. The reason for this procedure is that nitric acid is a very unpleasant substance to transport by road or rail. It has to be carried in special tank wagons and any leakage of such a corrosive liquid might be fraught with dangerous consequences. Sodium nitrate, on the other hand, is a neutral solid, whose transportation by road or rail does not give rise to any special difficulties. Sodium nitrate is, however, somewhat hygroscopic.

As an example of other modern processes for the fixation of atmospheric nitrogen, the cyanamide process may be mentioned. In this process ammonia is formed by the hydrolysis of calcium cyanamide (CaN.CN, from calcium carbide and nitrogen under pressure) by steam in autoclaves at 11 ats and 180° C.

$$CaN.CN + 3H_2O \rightarrow CaCO_3 + 2NH_3.$$

Hitherto power costs have prevented the adoption of the cyanamide process in this country.

The importance of the fixation of nitrogen cannot be overstressed. Had not the German chemist, Haber, discovered in 1913 how to obtain ammonia from hydrogen and nitrogen on the commercial scale, Germany could never have maintained her forces in the field until 1918. The allied blockade deprived the Central Powers of Chile saltpetre and other naturally occurring forms of combined nitrogen and, had Germany been dependent on these alone, she would soon have been unable to produce any more explosives.

Ammonium nitrate (NH_4NO_3)

This chemical was formerly made by the Freeth process, by the double decomposition of (Chile) sodium nitrate and ammonium sulphate (from gasworks and coke ovens). The Freeth process is now obsolete.

Ammonium nitrate is now made at Billingham (I.C.I.) by the direct neutralization of ammonia (from the Haber-Bosch process, *see* above) by nitric acid (from the Ostwald process).

$$NH_3 + HNO_3 + \text{water} \rightarrow NH_4NO_3 \text{ (aqueous)} + 12{\cdot}3K.$$

The neutralization takes place in towers, a hot solution of ammonium nitrate being drawn off at the bottom of the tower and allowed to crystallize in special vessels, which are rocked to prevent the formation of large crystals (the state of division of the ammonium nitrate used in making amatol is important). The resulting suspension of small crystals is centrifuged, in order to obtain solid ammonium nitrate.

Properties of ammonium nitrate.

Ammonium nitrate is a colourless crystalline salt, which melts at 170° C. when quite pure and dry. It exists in five different crystalline forms (α, β, γ, δ and ϵ). These forms undergo transition from one to another according to the temperature, if sufficient time is allowed for the transition to occur. The ranges of temperature, over which each of the five forms is stable, are perfectly definite. One of these transition temperatures is 32° C. (90° F.), which is of especial importance in the filling of shell with amatol. The β form, which is stable below 32° C., is denser than the γ form, which is stable above 32° C. Amatol fillings of shell tend, therefore, to shrink on cooling. An air gap may thus be introduced into the detonating system, so breaking its continuity and rendering it inefficient or even abortive.

In making hot mixed amatol, the strains produced in the crystals of ammonium nitrate at the γ–δ transition point 84° C. (184° F.) assist in reducing the material to a fine powder.

Ammonium nitrate reacts with most of the common metals, although the reaction with aluminium is practically negligible. With iron and lead it forms insensitive salts, which are harmless from the explosives point of view. Ammonium nitrate forms, with copper and tin alone, salts which are somewhat sensitive, but, when the copper and tin are together as in bronze or gunmetal, and especially if copper is tin plated, a still more sensitive compound is formed. This was a cause of accident in the early days of amatol manufacture when, following on the practice of gunpowder factories, bronze tools were used. These reactions with metals occur more readily in presence of *moisture*, and are, of course, more vigorous at elevated temperatures. It is essential, therefore, that amatols be kept dry.

Ammonium nitrate is graded by analysis into three grades, I, II and III. The chief impurities are :

(i) Moisture.
(ii) Saline impurities.
(iii) Pyridine (C_5H_5N).
(iv) Thiocyanates (*e.g.* sodium thiocyanate NaCNS).
(v) Acidity.

These impurities [(ii)–(v)] occur in gasworks or coke oven ammonium nitrate and *not* in the I.C.I. product from Billingham.

(i) The presence of too much moisture is undesirable for two reasons :

(*a*) In filling by the method of hot mixing or pouring, steam may be formed, which will tend to lower the density of the filling.

(*b*) In a filled shell, moisture absorbed by, or already present in, the ammonium nitrate may cause a softening of the filling owing to the partial solution of the ammonium nitrate. This may result in a form of exudation.

(ii) The chief saline impurities are sodium nitrate and sulphate and ammonium sulphate.

They are deliquescent and cause instability in the amatol.

(iii) and (iv) Pyridine and thiocyanates are introduced with ammonia derived from the distillation of coal. They are a fruitful cause of *exudation*. With the unsymmetrical trinitrotoluenes they form gaseous products. These give rise to frothing either during or after filling. In the former case the density of filling is reduced, which is likely to cause a set back on discharge, with the consequent danger of " blinds " ; in the latter case exudation follows. The resulting gases set up a pressure, which forces out the liquid exudation products, particularly at high temperatures of storage.

This is undesirable and dangerous, as the exudation products may affect the exploder system and render it inert, or, if the shells are not carefully cleaned, remain on the outside of the shell or in screw threads and invite prematures. For this reason particular care has to be taken that amatol for use in hot climates is made from the purest ammonium nitrate and trinitrotoluene.

It follows from the above that, if the T.N.T. used for amatol is impure, the ammonium nitrate must be pure, and vice versa.

Ammonium nitrate enters into the composition of many explosives besides amatol and examples will be found elsewhere in this book.

It is itself an explosive, but requires a very intense and powerful initiation before explosion will take place.

Saltpetre (potassium nitrate KNO_3).

(i) This chemical was formerly obtained from India in large quantities (*see* above). Such crude saltpetre (90 per cent. KNO_3) must be purified by recrystallization before it is suitable for use in gunpowder.

(ii) " Conversion " saltpetre is obtained by a double decomposition between sodium nitrate and potassium chloride. The sodium nitrate may be obtained from Chile or from I.C.I., Billingham. Potassium chloride occurs in Carnallite ($KCl.MgCl_2.$ $(6H_2O)$, of which there are large deposits at Stassfurt in Germany.

The reversible reaction involved is :

$$KCl + NaNO_3 \rightarrow NaCl + KNO_3.$$

By suitable control of the temperature and concentrations of the mixed solutions most of the sodium chloride can be precipitated. On cooling, the potassium nitrate separates out. It contains, however, about 0·5 per cent. of magnesium chloride and a certain amount of sodium chloride. The percentage of chloride can be reduced to about 0·05 per cent. by further recrystallization from solutions in some of the wash liquors, and the purified saltpetres finally dried.

During the final recrystallization the solution is vigorously agitated in order to obtain the saltpetre in as fine a form as possible. This reduces the amount of grinding required before the saltpetre is incorporated in the gunpowder.

CHAPTER X

NITRIC ACID. SULPHURIC ACID. OLEUM. WASTE ACID RECOVERY.

Nitric acid mixed with sulphuric acid or oleum (sulphuric acid in which is dissolved an excess of sulphur trioxide) is used in the nitration of glycerine, cellulose, toluene, etc. These acids are, therefore, essential materials for the production of explosives. An account of their manufacture is given, therefore, in this chapter. After the completion of a nitration the mixed acids have become diluted with water (which is formed during nitration) and contains various impurities, such as sulphur dioxide and the oxides of nitrogen These waste acids are " recovered " by purification and reconcentration.

Nitric acid. (Aqua fortis, HNO_3.)

Nitric acid for explosives manufacture is made from sodium nitrate (synthetic nitrate from I.C.I., or Chile saltpetre). The manufacture of sodium nitrate is described in Chapter IX.

The following is a description of the Hart process for making nitric acid, this process being used at the Royal Naval Cordite Factory, Holton Heath.

Reaction. $NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$

$$\underset{\text{sodium nitrate}}{NaNO_3} + \underset{\text{Sulphuric acid}}{H_2SO_4} \rightarrow \underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Sodium bisulphate.}}{NaHSO_4}$$

The sulphuric acid is made in another part of the factory (*see* below).

Process. Each of a row of cast iron retorts is charged with 2½ tons of sodium nitrate and 2½ tons of concentrated sulphuric acid. The retorts are heated by producer gas and the reaction is allowed to proceed as is shown in the above equation. By doubling the charge of nitrate we could get double the amount of nitric acid from a given amount of sulphuric acid :

$$2NaNO_3 + H_2SO_4 \rightarrow 2HNO_3 + \underset{\text{Normal sodium sulphate.}}{Na_2SO_4}$$

This is *not* done, the reason being that sodium bisulphate is readily fusible and can be run off into crystallizing pans at the end of a heating. The normal sodium sulphate on the other hand would form a solid mass in the retort and its removal would entail a great expenditure of time and labour.

The vapours from the retorts pass through stoneware pipes to a collector, after which they are condensed in water-cooled coils of fused silica (SiO_2). The resulting distillate is a nitric acid of 94 per cent. strength. This would appear to be strange at first sight, for nitric acid and water form a mixture of constant boiling point which contains only 68 per cent. of nitric acid and boils at 121° C. The production of acid of 94 per cent. strength is, however, made possible by the fact that the sulphuric acid in the retort has a great affinity for water, which is thus largely prevented from distilling over with the nitric acid.

The by-product sodium bisulphate is crystallized out in large flat pans and is sold.

Properties of nitric acid.

(i) *Physical.* When free from water and from oxides of nitrogen, nitric acid is a colourless liquid of a specific gravity of 1·52 at 15° C. It boils with partial decomposition at 86° C. :

$$4HNO_3 \rightarrow \underset{\text{Oxygen}}{O_2}+\underset{\text{Nitrogen peroxide.}}{4NO_2}+2H_2O.$$

On distilling dilute nitric acid, water alone passes over and the solution becomes progressively richer in nitric acid until, when the acid contains 68 per cent. HNO_3, the whole distils at a constant temperature of 121° C., as though the 68 per cent. acid were a homogeneous liquid. This constant boiling mixture is the commercial acid of a specific gravity of 1·414. Conversely, when an acid of over 68 per cent. strength is distilled, it loses pure nitric acid with simultaneous rise of boiling point, until the constant boiling mixture again distils at 121° C.

(ii) *Chemical.* The decomposition of nitric acid on heating is important. During a nitration nitrogen peroxide is always formed, and must be removed from the waste acids. The ready liberation of oxygen from nitric acid makes it a powerful oxidizing agent, especially when concentrated.

The most important chemical property of nitric acid from the service point of view is its capacity for nitrating such substances as glycerine, toluene and phenol. The nitric acid replaces a hydrogen atom by the nitro-group (NO_2), water being formed simultaneously. Thus :

$$\underset{\text{Benzene}}{C_6H_5.}\boxed{H+HO.}\underset{\text{Nitric acid}}{NO_2} \rightarrow \underset{\text{Nitrobenzene.}}{C_6H_5NO_2}+H_2O.$$

Sulphuric acid is added to the nitric acid in order to absorb the water and prevent a dilution of the nitric acid, which would impair its effect as a nitrator.

Sulphuric Acid—Oleum

Sulphuric acid (oil of vitriol H_2SO_4) may be made either by (i) the lead chamber process, or (ii) by the contact process.

(i) *The Lead Chamber Process* depends on the interaction of sulphur dioxide with steam and air in the presence of oxides of nitrogen : $4HNO_3 \rightarrow 2H_2O + 2NO_2 + O_2$.

1. $\underset{\text{Nitrogen peroxide}}{NO_2} + \underset{\text{Sulphur dioxide}}{SO_2} \rightarrow \underset{\text{Nitric oxide}}{NO} + \underset{\text{Sulphur trioxide.}}{SO_3}$
2. $SO_3 + H_2O \rightarrow H_2SO_4$
3. $2NO + O_2 \rightarrow 2NO_2$., and so on.

The nitrogen peroxide is regenerated (equation (3)) so that, in theory, a small quantity of nitric acid should give an infinite amount of sulphuric acid. In practice, there is wastage of nitrogen peroxide and one ton of nitric acid is used up for every 30 tons of sulphuric acid that are formed.

The lead chamber process gives directly an acid of only about 70 per cent. strength and will not be described in detail in this book.

(ii) *The contact process.* The process depends on the fact that, when sulphur dioxide and oxygen (air) are passed over a catalyst at about 450° C., sulphur trioxide is formed :

$$2SO_2 + O_2 \rightarrow 2SO_3 \text{ (sulphur trioxide).}$$

This reaction is reversible and the equilibrium mixture contains less sulphur trioxide as the temperature is raised. On the other hand the rate at which equilibrium is attained increases with rise of temperature. It is necessary, therefore, to strike a balance between the above factors. The optimum temperature of reaction is found to be about 450° C.

There are various types of catalyst used :

(*a*) In the Tenteleew process finely divided platinum is used. This catalyst is, however, " poisoned " by traces of arsenic, so the reacting gases must be carefully purified from arsenic before passage over the catalyst.

(*b*) The Grillo process uses 0·3 per cent. of platinum on magnesia (calcined magnesium sulphate).

(*c*) The Mannheim process uses burnt pyrites cinder (Fe_2O_3) as the primary catalyst. This catalyst has the great advantage that it is not affected by dust or arsenic.

(*d*) The Selden process uses a catalyst composed of vanadium oxide.

The resulting sulphur trioxide is absorbed in 98 per cent. sulphuric acid (which absorbs SO_3 more readily than pure water). If it be desired to obtain sulphuric acid, water is added in proportion :

$$SO_3 + H_2O \rightarrow \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

If, on the other hand, it is desired to obtain oleum (fuming sulphuric acid), no water is added. The 98 per cent. sulphuric acid is first dehydrated by the sulphur trioxide and gives anhydrous acid. Further addition of sulphur trioxide gives oleum. In this way an acid containing up to 40 per cent. of free sulphur trioxide may be readily obtained.

The Tenteleew (Tentelef) process is used at the Royal Naval
am 1 Cordite Factory and will ~~not~~ now be described in detail (Fig. 10.1).

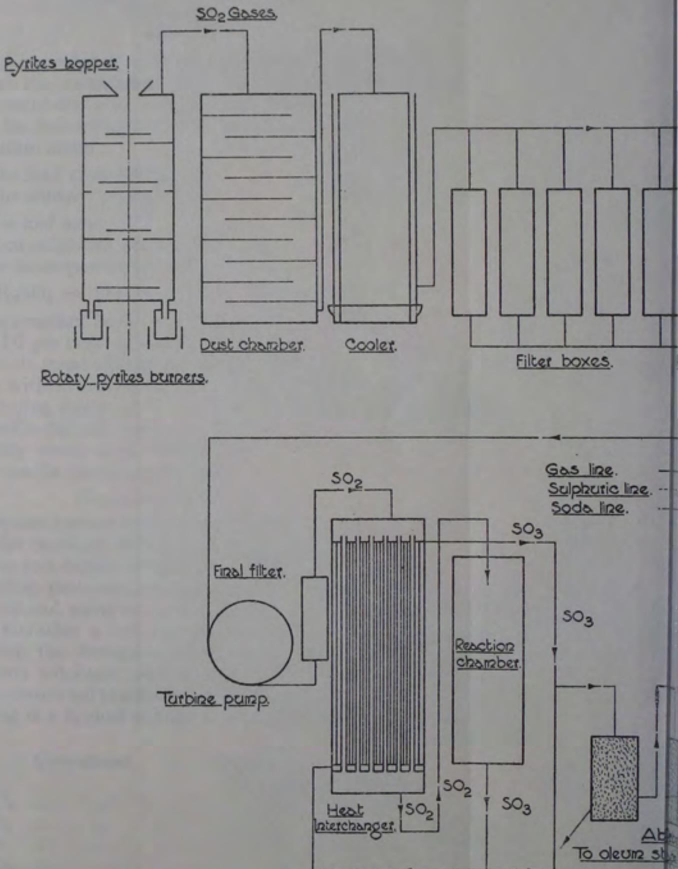
Iron pyrites ($Fe.S_2$) are fed from a hopper into a rotary pyrites burner. This is a brickwork chamber, about 12 feet in diameter and 10 feet high. At the bottom of the burner is a grate. A fire is lit in the grate to start the combustion of the pyrites. Once the pyrites are well alight, the heat generated by their combustion suffices to keep the reaction going :

$$\underset{\text{Iron pyrites}}{4FeS_2+11\,O_2} \rightarrow \underset{\text{Ferric oxide.}}{2Fe_2O_3+8SO_2.}$$

A controlled supply of air is admitted through openings in the side of the burner. The burner is divided into a series of " floors " by horizontal partitions. These partitions have openings alternately at the periphery and at the centre, the openings allowing pyrites to fall from one floor to the next. Passing up the centre of the burner is a vertical shaft which is driven at a speed of about one revolution a minute by suitable gearing.

Attached to this shaft are long arms or " rabbles ", a set for each " floor ". The rabbles carry teeth which are arranged on alternate floors to work the charge of burning pyrites towards the centre and the outside of the burner, respectively. The mechanical action which occurs in the burner is as follows :

Pyrites from the hopper fall on to the top " floor ". The rabbles on this floor force the pyrites towards the centre, whence they fall on to the next lower floor. The rabbles on this second floor force the pyrites from the centre to the outside, whence they fall to the third floor, and so on. The pyrites cinder (Fe_2O_3) is withdrawn at the bottom of the burner. The gaseous products of combustion (sulphur dioxide and unchanged air) are withdrawn from the top of the burner by means of a wide pipe, which leads to a dust chamber. The gases pass down this chamber over baffle plates, which serve to remove pyrites dust, etc., from the gas. The gas now passes through a cooler, then through lead filter boxes which are packed with quartz. Passage through the soda-tower removes arsenic (derived from the pyrites) as sodium arsenite (Na_3AsO_3). The gas is now passed up drying towers down which trickles concentrated sulphuric acid. Next comes a turbine pump and then a final filter, which removes any pump oil that may have got into the gas. The gases then pass through a heat interchanger, where they are heated at the expense of the hot gas from the reaction chamber. This is packed


SO2 Gases.
Pyrites hopper.
Rotary pyrites burners.
Dust chamber.
Cooler.
Filter boxes.
Gas line.
Sulphuric line.
Soda line.
SO2
SO3
Final filter.
Turbine pump.
Reaction chamber.
Heat Interchanger.
SO2
SO3
SO2
SO3
SO3
SO3
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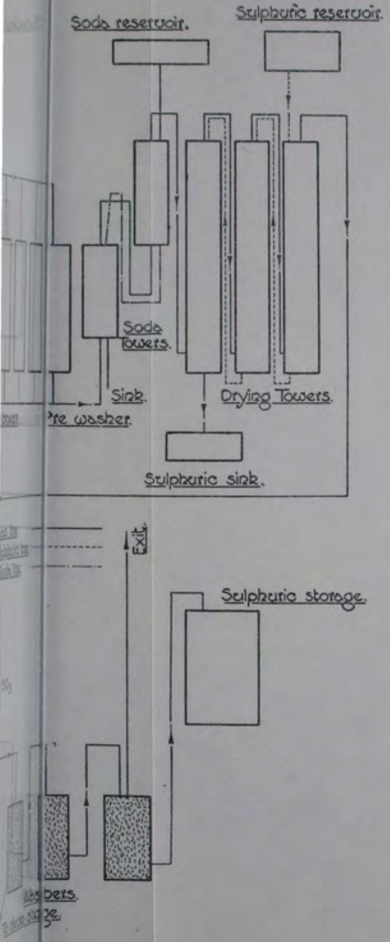
To oleum st

FIG. 10.1.

[*To face page* 68.



with asbestos impregnated with 7 per cent. of platinum. Here sulphur trioxide is formed :

$$2SO_2 + O_2 \xrightarrow[450^\circ\ \text{C.}]{} 2SO_3 + 64{\cdot}3\text{K.}$$
$$\text{Platinum}$$
$$450^\circ\ \text{C.}$$

The resulting sulphur trioxide passes, a part via the heat interchanger and the remainder direct to the absorbers, where it is absorbed in sulphuric acid of 98 per cent. strength.

In 1934 the following quantities of sulphuric acid were produced in Great Britain alone :

By the lead chamber process ...	750,000 tons.
By the contact process	200,000 tons.

Properties and uses.

Anhydrous sulphuric acid, H_2SO_4, has a specific gravity of 1·84. It boils with decomposition at 330° C. :

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_3 \rightarrow 2H_2O + 2SO_2 + O_2.$$

and forms a constant boiling mixture which contains 98·3 per cent. of acid and 1·7 per cent. of water.

Owing to its great affinity for water (with which it forms a series of hydrates with evolution of much heat) sulphuric acid is largely used as a drying agent and to absorb water formed in nitration. Oleum is used in difficult cases, *e.g.* the preparation of trinitrobenzene and to fortify weak acids from waste acid recovery. Oleum is also widely used in the dyestuffs industry.

The recovery of Waste acids.

An important feature in the economical working of any explosives factory is the recovery of waste acids, and their purification and concentration to a degree suitable for further use.

In nitrating processes a mixed acid consisting of nitric acid, sulphuric acid and water in various proportions is used.

During nitration a considerable amount of the nitric acid is used up, with the formation of an equivalent amount of water. Further, some sulphuric acid is lost in side reactions and some nitric acid is converted to nitrous acid (HNO_2) and oxides of nitrogen. The following is a typical change in composition of the acid during nitration.

Constituent.	*Mixed acid*	*Waste acid*
	Per cent.	*Per cent.*
H_2SO_4	80	72
HNO_3	18	0
H_2O	2	25
HNO_2	0	3
	100	100

The flow sheet for acids used in an explosives factory is shown in Fig. 10.2.

The methods adopted for acid recovery are governed mainly by the degree of dilution of the waste acids. Generally, the following courses are open :

am 1 (i) To use the waste acids, as collected, for some other operation for which they may be suitable, *e.g.* in the super-~~detonator~~ detoluator of a T.N.T. plant (*see* Chapter XVIII).

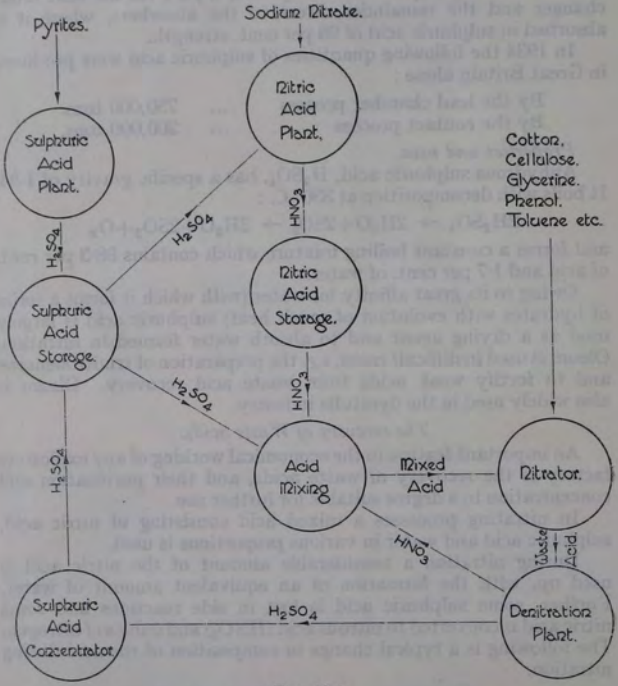


FIG. 10.2.

(ii) To add fresh strong acids to the waste acids until the final product has the required composition.

(iii) To separate and concentrate the constituents of the waste acids with a view to their addition to the main supply of fresh acids. This is the method adopted in dealing with acids surplus to requirements under heads (i) and (ii) above and is the subject for discussion in this chapter.

The separation of the nitric acid from the sulphuric acid is

HIGH TEMPERATURE DENITRATING COLUMN.

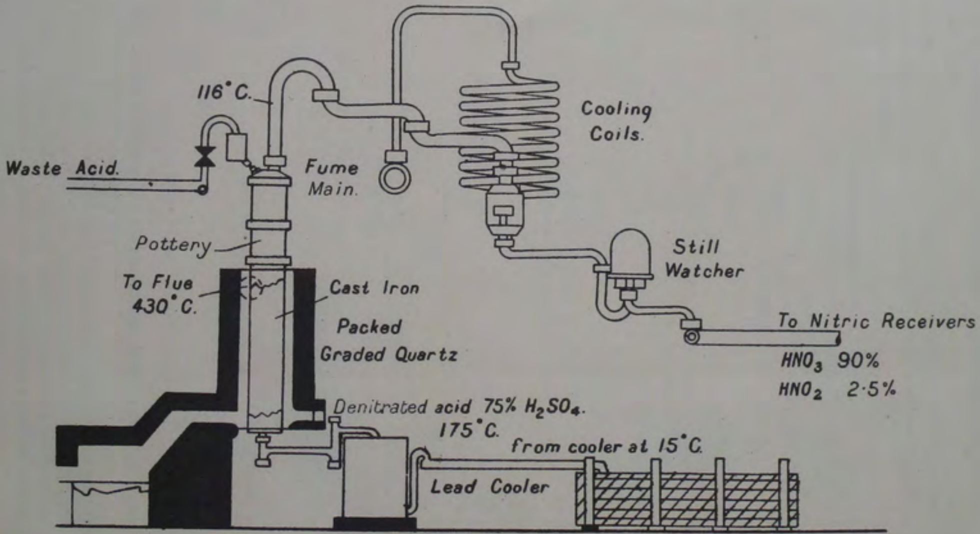


FIG. 10.3

Malby & Sons, Lith.

generally known as the *denitration* of the waste acids and it is the essential preliminary to concentration. Direct concentration of the waste acids is impracticable owing to the excessive corrosion of the plant by the nitric acid.

Procedure.

1. *Denitration.* There are two types of denitrator, (*a*) denitrating stills and (*b*) column denitrators.

(*a*) *Denitrating stills.* These are similar to the retorts used in the manufacture of nitric acid. The waste acids are heated in the still to about 110° C. The nitric acid passes over with a large amount of steam and is condensed, cooled and collected in the usual manner (*see* above under nitric acid).

(*b*) *Column denitrators* (Fig. 10.3). These are of two types :

(i) Low-temperature column denitrators.
(ii) High-temperature column denitrators.

Both types comprise the following :

1. A feed tank.

2. A denitrating column of acid-proof material, packed with quartz.

(i) Low-temperature columns are built of acid-proof bricks, contained in a steel case. Super-heated steam is used as the source of heat.

(ii) High-temperature columns are made of acid-proof cast-iron (Ni-resist) and are heated externally by hot furnace gases.

3. Condensers and absorbtion towers.

The nitric acid, and the nitrous acid which is always associated with it, are driven off and partially dissociated according to the following equations :

$$4HNO_3 \rightarrow 4NO_2+2H_2O+O_2$$
$$2HNO_2 \rightarrow H_2O+NO+NO_2.$$

The unchanged acids are condensed, while the oxides of nitrogen pass on to the absorbtion towers. In these towers the oxides are absorbed, the lower oxide being converted to nitrogen peroxide (NO_2). Nitrous and nitric acids are formed :

$$2NO+O_2 \rightarrow 2NO_2$$
$$H_2O+2NO_2 \rightarrow HNO_2+HNO_3.$$

This process of oxidation is not instantaneous. A sufficiency of oxygen in the form of air is the first essential ; the second is adequate time for the reaction to proceed to completion. The nitric acid collected in the manner just described is dilute, but its further concentration is not difficult. The nitrous acid (HNO_2), being unstable, breaks up into water and oxides of nitrogen, from which, by further oxidation, nitric acid is formed.

Denitrated acid is collected from the bottom of the denitrating column, cooled and stored for concentration. It contains about 75 per cent. sulphuric acid, the remainder being chiefly water.

The waste acids from the nitration of glycerine and the manufacture of picric acid, T.N.T., etc., may be concentrated in low temperature denitrators ; but those from the nitration of cellulose must be denitrated in stills or high temperature columns, as they contain non-volatile substances which are not readily decomposed by super-heated steam and which would clog the packing of the column.

2. *Concentration of denitrated acid.* There are three main types of sulphuric acid concentrators :

(*a*) *Kessler concentrators.* These are useful in small works where the amount of acid to be treated is not large or where working is intermittent.

The concentrator (Figs. 10.4 and 10.5) consists of a small tower of acid-proof brickwork, in which trays of the type shown in Fig. 10.4 are mounted. The weak acid enters at the top and descends from tray to tray against a stream of hot furnace gases. During its passage through this portion of the concentrator the acid is heated and partially concentrated.

The descending stream of acid is collected in a large trough at the base of the tower and the final concentration is accomplished by the heat from the hot furnace gases as they impinge on the surface of the liquid. The strong acid is then run off into coolers and is finally stored.

The Evans-Bowden tower. (Fig. 10.6.)

This was invented by Dr. Bowden, of the Royal Gunpowder Factory, and is a great improvement on the Kessler tower. It is made of Staffordshire blue brick and costs only £40 for bricks as against £600 for the volvic stone which is used in the Kessler tower. The bricks are bound together with a cement of glass powder, sodium silicate (water glass) and pumice powder, which sets to a hard, durable binding.

An Evans-Bowden tower will deal with three times as much waste acid as will a Kessler tower.

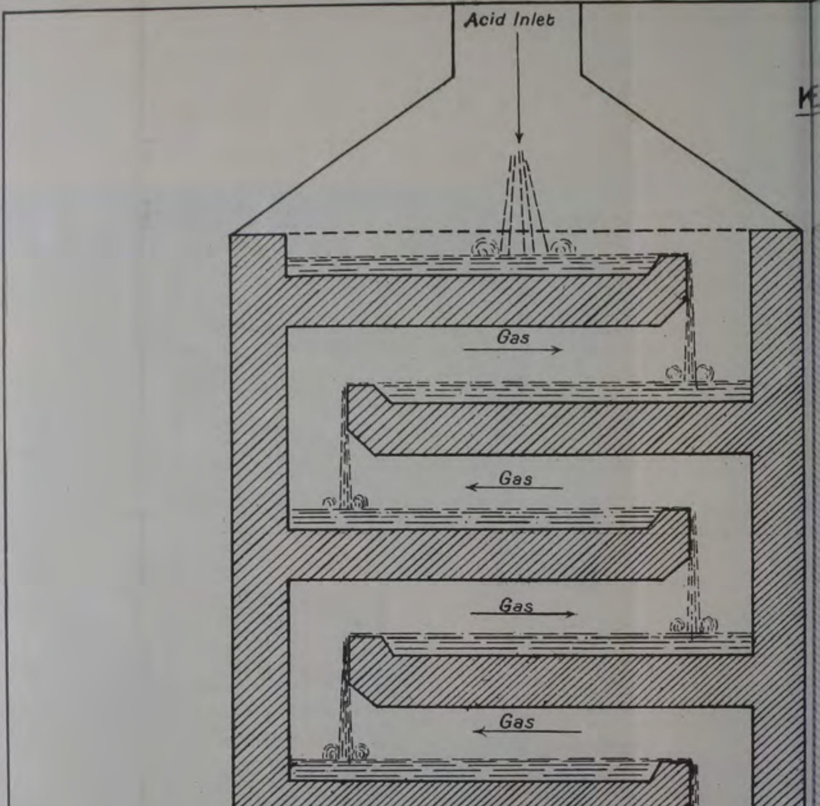
The great feature of the former is the alternate rows of arches and half-arches (Fig. 10.6) over which the denitrated acid has to flow in its passage down the tower. The flow is from centre to outside on a full arch and from outside to centre on a pair of half-arches.

(*b*) Gaillard towers.

(*c*) Gilchrist towers.

These are operated in much larger units than (*a*) above and are the best where large quantities of acid have to be handled.

The concentrated sulphuric acid obtained by any of the above methods is of 96–97 per cent. strength.



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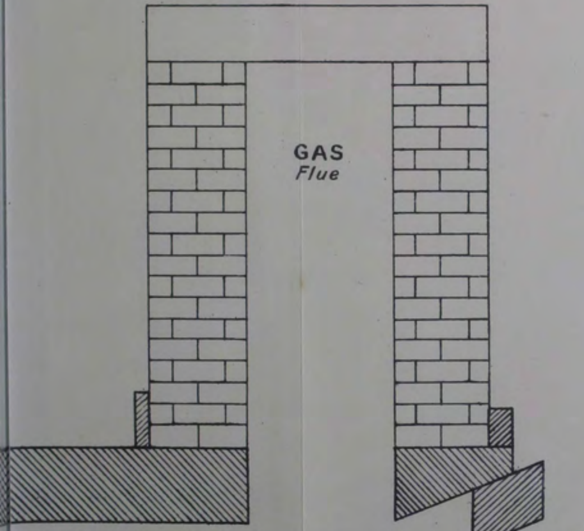
SSLER SULPHURIC ACID CONCENTRATOR.

FIG. Nº 10.4.



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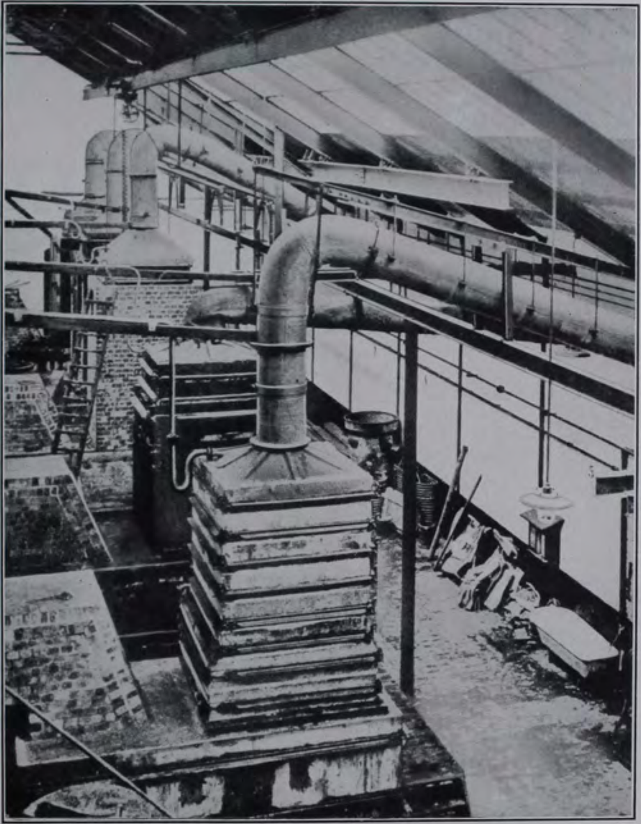


FIG. 10.5.

3. *Recovery of acid fumes.* These have to be recovered, both in the interests of economy and in order to prevent a nuisance to the environs of the factory.

These fumes may be recovered either in absorbtion chambers or by the Cottrell electrostatic precipitator. This precipitator contains a large number of vertical metal tubes, each of which carries a central wire, the wires being kept taut by suspended weights.

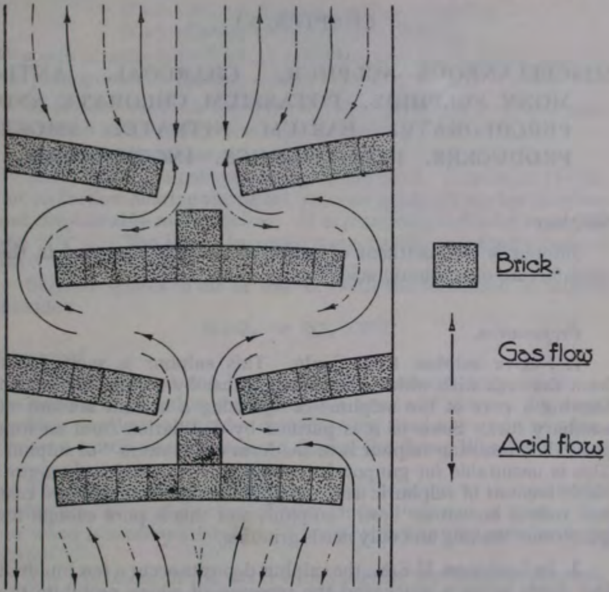


FIG. 10.6.

A potential difference of 60 kilovolts is maintained between the wires and tubes in such a manner that the charged particles of sulphur trioxide and acid coalesce on the inside of the tubes, whence they fall down into a sump.

CHAPTER XI

MISCELLANEOUS—SULPHUR. CHARCOAL. ANTIMONY SULPHIDE. POTASSIUM CHLORATE AND PERCHLORATE. BARIUM NITRATE. SMOKE PRODUCERS. PYROTECHNICS. INCENDIARIES.

Sulphur

Sulphur is a constituent of gunpowder and is also used in the manufacture of sulphuric acid.

Preparation.

1. Native sulphur from Sicily. This sulphur is melted out from the rock with which it is mixed, either by setting fire to and burning a part of the sulphur, or by using a certain amount of auxiliary fuel. Some of it is purified by distillation from an iron pot. The resulting sulphur is in the form of " flowers " of sulphur. This is unsuitable for gunpowder making, as it contains an appreciable amount of sulphuric acid. Sulphur which is melted and cast into rods is known as " roll " sulphur, and this is pure enough for gunpowder making and only needs grinding.

2. In Louisiana, U.S.A., the sulphur deposits occur a few hundred feet down below a quicksand the presence of which prohibits the use of ordinary methods of mining. The sulphur, therefore, is won by the Frasch process, in which superheated steam is forced down one of a series of concentric pipes. The sulphur is thereby melted. Compressed air is used to drive the molten sulphur through another of the pipes. The molten sulphur flows into colossal bins, where it solidifies in masses of up to 150,000 tons. The solid sulphur is blasted, quarried by means of excavators and loaded into railroad trucks. The resulting sulphur has a purity of from 99·93 to 99·98 per cent.

3. In Germany, during the Great War, there was an acute shortage of sulphur owing to the allied blockade. The Germans, therefore, evolved the Claus-Chance process, whereby sulphur was obtained from gypsum (calcium sulphate, $CaSO_4\ 2H_2O$), a mineral which is found in Germany.

The gypsum was reduced to calcium sulphide by heating with coke or charcoal :

$$CaSO_4, 2H_2O+4C \rightarrow CaS+2H_2O+4CO.$$

The calcium sulphide, in the presence of air and carbon dioxide, gave sulphur :

$$2CaS+3O_2 \rightarrow 2CaSO_3 \text{ (calcium sulphite).}$$
$$2CaS+CaSO_3+3CO_2 \rightarrow 3S+3CaCO_3.$$

Deposits of anhydrite ($CaSO_4$) at Billingham are utilized thus for the production of sulphuric acid.

4. Recent work on the recovery of sulphur from furnace gases may give a useful indigenous source of sulphur.

Properties of sulphur.

Roll sulphur is a pale yellow crystalline solid. It melts at 114° C., but on further heating the liquid becomes gradually darker in colour and considerably more viscous. It is practically solid between 160° and 220° C. The liquid becomes more mobile and finally boils at 444·5° C.

Sulphur ignites in air at 260° C., with the formation of sulphur dioxide :

$$S+O_2 \rightarrow SO_2+70K.$$

Charcoal

Soft woods give the best charcoal for use in gunpowder. In the service dogwood is employed as a source of charcoal for rapid burning powders, and alder or willow for the large grain powders. Cheaper woods were introduced during the Great War to augment the supply.

The wood requires careful selection. It is cut in the spring for preference, as at that time of year the ash content is least. The cut wood is seasoned for 1½ to 3 years, either in the open or under thatch.

The treatment of the wood varies slightly for different powders, but in general the procedure followed is as described below.

(i) The wood is packed in an iron cylinder. The cylinder is placed in a retort, fitted with a delivery pipe, and heated for 3½ to 6 hours. The volatile products of distillation escape by the delivery pipe and, after recovery of by-products, are used to assist in heating the furnace.

(ii) The cylinder and its contents are then allowed to cool out of contact with air, since the hot ready-made charcoal is very inflammable. After a week has elapsed, air is gradually admitted to the charcoal. This must be done slowly, as charcoal absorbs oxygen very readily, and with so great an evolution of heat that ignition may occur.

Charcoal for service powders should be jet black in colour, have a clear velvet like surface on fracture, and be so soft that it will not scratch polished copper.

The usual yield is from 28 to 29 per cent. of the dried wood.

An average analysis for black charcoal is :

Carbon	81 per cent.
Hydrogen	3 per cent.
Oxygen	14 per cent.
Ash	2 per cent.
	100

Brown charcoal.

This was used for the brown or " cocoa " powders. It is made from rye straw by charring with superheated steam. It yields a soft charcoal of a brown colour, which contains a much higher percentage of hydrogen and oxygen than the ordinary black charcoal.

Under pressure, this brown charcoal coalesces and, in the gunpowder in which it was used, binds the other constituents together into a dense impervious mass. The " cocoa " powders gave the best ballistics of any powder used as a propellant, but were inferior, of course, to the smokeless propellants which have superseded them.

Antimony Sulphide (Sb_2S_3)

This is used in detonating and cap compositions, in order to prolong the flame effect.

It occurs naturally as the mineral stibnite or antimonite, and is noted for its brilliant metallic lustre, black colour and low melting point (555° C.), which makes it possible to concentrate the sulphide, by fusion, from the accompanying earthy impurities.

Potassium Chlorate ($KClO_3$). Potassium Perchlorate ($KClO_4$)

Potassium chlorate is used in detonating, cap and fulminate compositions. Potassium chlorate and perchlorate are both used in various explosives, of which examples will be found elsewhere in this book.

Potassium chlorate may be prepared in Commerce :

(i) By bubbling chlorine through milk of lime heated to 40° C. in cast iron cylinders fitted with agitators, giving a solution of calcium chloride and chlorate :

$$\underset{\text{Calcium hydroxide}}{6Ca(OH)_2}+6Cl_2 \rightarrow \underset{\substack{\text{Calcium}\\\text{chloride}}}{5CaCl_2}+\underset{\substack{\text{Clacium}\\\text{chlorate.}}}{Ca(ClO_3)_2}+6H_2O$$

After filtration the concentrated solution was decomposed by the addition of potassium chlorate on cooling

$$Ca(ClO_3)_2+2KCl \rightarrow CaCl_2+2KClO_3.$$

5/6ths of the chlorine is employed in producing the valueless calcium chloride, but there is no serious waste of potassium.

(ii) *Electrolytic oxidation.* This is much cheaper than the old chlorine process and is now used where electric power is available.

An aqueous solution of potassium chloride is electrolyzed at 60°–70° C., under conditions which allow the cathode and anode products to mingle freely. Under these conditions potassium chloride is oxidized at the anode to potassium chlorate, whilst hydrogen gas is evolved at the cathode, the general result of the electrolysis being expressed by the equation :

$$KCl+3H_2O \rightarrow KClO_3+3H_2$$

By further electrolytic oxidation in a separate vat, potassium perchlorate is obtained.

Properties.

Potassium chlorate melts at 370° C. and, on further heating, decomposes with effervescence, liberating oxygen, probably according to the equations :

$$\begin{aligned} 4KClO_3 &\rightarrow 3KClO_4+KCl \\ KClO_4 &\rightarrow KCl \quad +2O_2. \end{aligned}$$

In the presence of small quantities of various oxides, the decomposition of the chlorate occurs at 200° C. without fusion and no perchlorate is formed.

$$2KClO_3 \rightarrow 2KCl+3O_2.$$

Owing to its powerful oxidizing action, potassium chlorate is used in many explosives. An attempt to use it in place of saltpetre for making gunpowder led, in 1788, to a fatal explosion in France.

Potassium perchlorate is also used in explosives. Although it contains a higher percentage of oxygen than the chlorate, it is less violent in its action.

Barium Nitrate ($Ba(NO_3)_2$)

This chemical is of some importance owing to its density and non-hygroscopic nature. It is, therefore, used as a constituent of baratol (*see* Chapter XVIII) for the filling of grenades.

The green colour which barium salts impart to a flame makes barium nitrate of great use as an oxidizing agent in pyrotechnics and signal compositions (Chapter XXIII).

Barium nitrate is made by dissolving witherite (Barium carbonate $BaCO_3$, a home-produced mineral) in hot nitric acid and evaporating to the crystallizing point.

$$BaCO_3+2HNO_3 \rightarrow Ba(NO_3)_2+H_2O+CO_2.$$

Smoke Producers

The following chemicals are of use, either alone, or in compositions, as smoke producers :

(*a*) *White phosphorus.* The element phosphorus occurs in two principal forms :

(i) White phosphorus, which is very inflammable.

(ii) Red phosphorus, which can only be ignited with difficulty.

White phosphorus is prepared from calcium phosphate, sand and coke in an electric furnace,

$$\underset{\text{Calc. phosphate.}}{2Ca_3(PO_4)_2}+\underset{\text{Sand}}{6SiO_2}+10C \rightarrow \underset{\text{Phosphorus.}}{P_4}+\underset{\text{Calc. silicate}}{6CaSiO_3}+\underset{\text{Carbon monoxide.}}{10CO.}$$

The crude phosphorus is melted under hot water (owing to its inflammable nature) filtered through a canvas bag, and cast into wedges or sticks which are packed under water in soldered tins.

Properties.

White phosphorus is a pale yellow solid, which melts at 44° C. It is terribly poisonous, the lethal dose being about 1½ grains. Constant exposure to its vapour leads to necrosis of the jaw (" phossy jaw "). It has been found that, by keeping the phosphorus moist, it may be handled with reasonable safety by the workers.

Phosphorus is very inflammable and burns to phosphorus pentoxide (P_4O_{10}) with the evolution of much heat :

$$P_4+5O_2 \rightarrow P_4O_{10}+370K.$$

The phosphorus pentoxide gives a dense white smoke ; hence the use of phosphorus in smoke shell. The heat of the hand is often sufficient to cause white phosphorus to inflame. This chemical, therefore, should only be handled with tongs, as phosphorus burns are very painful and difficult to heal.

On account of its inflammability service stores containing white phosphorus are always kept in separate explosives stores. When transported by sea, such stores may only be carried as deck cargo (*see* " Magazine Regulations ").

Hexachlorethane (C_2Cl_6)

Calcium Silicide (Ca_2Si)

Zinc Oxide (ZnO)

These three chemicals are used in lieu of white phosphorus in various smoke compositions, *e.g.* in smoke shell of the base ejection type.

Pyrotechnics

The following chemicals are used in pyrotechnic compositions :

Sodium nitrate ($NaNO_3$)—gives a yellow flame.
Strontium nitrate ($Sr(NO_3)_2$)—gives a red flame.
Barium nitrate $Ba(NO_3)_2$—gives a green flame.
Basic copper carbonate $CuCO_3.Cu(OH)_2$ for blue star.

Lactose or milk sugar, $C_{12}H_{22}O_{11}$, which is obtained from milk.

Various dyestuffs to give coloured smokes for daylight signalling purposes.

Incendiaries

Aluminium powder. Powder aluminium burns with the evolution of intense heat.

$$4Al+3O_2 \rightarrow \underset{\text{Aluminium oxide.}}{2Al_2O_3}+2\times380K.$$

If mixed with powdered magnetic oxide of iron, aluminium powder gives thermit (*see* Chapter I).

Magnesium powder also gives intense heat on combustion.

$$2Mg+O_2 \rightarrow \underset{\text{Magnesia.}}{2MgO}+2\times143K.$$

D.—MANUFACTURE OF PROPELLANTS AND SUBSTANCES ENTERING INTO THEIR COMPOSITION

CHAPTER XII

NITROGLYCERINE N./G.

Introduction.

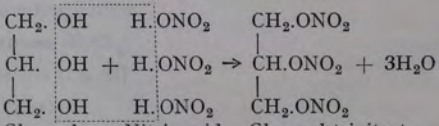
The name " nitroglycerine " is a misnomer, for this substance is really the trinitrate (or nitric ester) of glycerol. (Chapter VII.) Its chemical name is " glyceryl trinitrate " or " trinitrin ". The prefix " nitro " can only strictly be applied to bodies which contain the nitro-group (NO_2) as opposed to the nitrate group ($O.NO_2$). True nitro-bodies are :

Nitrobenzene $C_6H_5.NO_2$ (Chapter VIII).
Nitromethane $CH_3.NO_2$.

An example of a nitrate, on the other hand, is ethyl nitrate, $C_2H_5.O.NO_2$, which is derived from ethyl alcohol $C_2H_5.OH$.

Nitroglycerine was discovered by Sobrero in 1846, and its manufacture on a commercial scale started in Sweden about 1860. It is a constituent of most modern propellants and of many mining explosives.

Nitrogylcerine is readily formed by the action of nitric acid on glycerine :



$$\begin{array}{lllll} CH_2.OH & & H.ONO_2 & & CH_2.ONO_2 \\ | & & & & | \\ CH.OH & + & H.ONO_2 & \rightarrow & CH.ONO_2 + 3H_2O \\ | & & & & | \\ CH_2.OH & & H.ONO_2 & & CH_2.ONO_2 \end{array}$$

Glycerol. Nitric acid. Glyceryl trinitrate or nitroglycerine.

If the above molecular proportions are used, the reaction will *not* proceed to completion, owing to the dilution of nitric acid by the water which is formed. In manufacture this water is removed as rapidly as it is formed by the addition of sulphuric acid to the nitric acid. The action then proceeds readily, with considerable evolution of heat.

When nitroglycerine is detonated, the resulting products are entirely gaseous :

$$4C_3H_5(NO_3)_3 \rightarrow 12CO_2+10H_2O+6N_2+O_2.$$

Nitroglycerine is thus remarkable in that it contains more oxygen than is needed for its complete combustion.

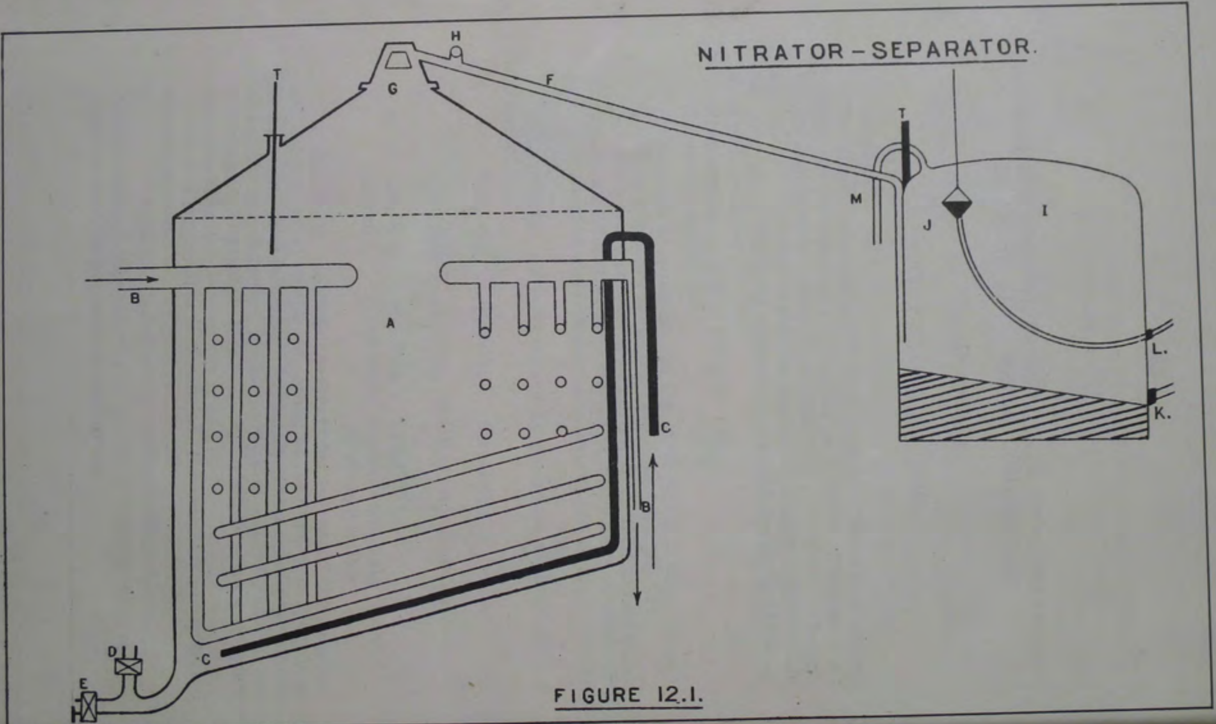


FIGURE 12.1.

Owing to its great sensitivity nitroglycerine may *not safely* be pumped through pipes, nor may its flow be controlled through stop-cocks, in which some of the nitroglycerine may get pinched. In manufacture it is passed from vessel to vessel by canvas-covered lead gutters, connections being by hose pipe, where needed, and the whole flow being controlled by gravity.

Manufacturing vessels are all made of lead and, when transportation by hand is necessary, this is done in rubber vessels.

Manufacture of nitroglycerine

1. The Royal Gunpowder Factory, Waltham Abbey, uses the Rintoul-Nathan process, which is described below.

(*a*) *Nitration.* The glycerol is nitrated in a Rintoul-Thomson nitrator-separator (Fig. 12.1.) This consists of a lead vessel (A) with a sloping bottom, fitted with a cooling coil system (B), in which is circulated brine at a temperature below 0° C., and an air stirrer (C) for continually agitating the contents by blowing air through them. Pipes (D) and (E) communicate with the bottom of the vessel ; the former is an inlet for both nitrating and displacement acids, as well as an outlet for displacement acid, whilst the latter communicates with a " drowning tank " into which the contents of the nitrator are evacuated should the chemical reaction within it get out of hand and the temperature, as observed by a thermometer (T), become dangerously high.

The top of the vessel is conical and is fitted with an overflow pipe (F) leading to the " pre-wash " tank (I). A glass sight window (G) is let in at the level of the overflow pipe and a fume exhaust connected to the latter at (H). The " pre-wash " tank is a lead vessel with a sloping bottom and is fitted with arrangements for air stirring.

A charge of 2·6 tons of mixed nitrating acid is run into the nitrator. The composition of the mixed acid is :

	Per cent.
Sulphuric acid	59
Nitric acid	39
Water	2

This will completely nitrate 1,400 lb. of glycerol, producing about 2,600 lb. of nitroglycerine.

The acid is stirred by the injection of air and cooled by the brine coils to below 12° C. The above quantity of glycerol is then slowly introduced through the top of the nitrator. It is projected into the continually cooled and stirred acid in the form of a fine spray from an air injector. There is a great evolution of heat and the temperature of the contents of the nitrator must be controlled by means of the brine cooling, air stirring and regulation of the rate of glycerol injection. The temperature of the contents must be kept well below 22° C., although it is normally only about 10° C. ; should this temperature (22° C.) be accidentally reached, the whole of the charge must be " drowned " in a large lead vessel containing water provided for this purpose. The nitration of the above quantities occupies about 45 minutes. The contents are then cooled to about 15° C. and the air shut off to allow the nitroglycerine to separate.

(*b*) *Separation.*

The nitroglycerine is lighter than the nitrating acid, and in about 20 minutes has for the most part separated into an oily layer on the surface of the latter. Waste acid from a former charge is now slowly introduced into the bottom of the nitrator until the nitroglycerine overflows through the pipe (F) into the " pre-wash " tank (I). The flow is watched through the sight window and is stopped before any quantity of nitrating acid escapes. The waste acid is then run out of the nitrator into two acid " eggs " " A " and " B ", the acid from egg " A " being used for the displacement of a subsequent charge and that from egg " B " going to the acid recovery plant, where the nitric and sulphuric acids are separated and recovered. The acid eggs are worked by compressed air. The nitrator is then ready for the next charge.

The waste acid is diluted with about 5 per cent. of water after the completion of the nitrating process.

This is done for two reasons :

(*a*) To precipitate all nitroglycerine from the waste acid before separation, and

(*b*) to prevent after nitration of mono- and dinitroglycerine, traces of which might be present in the waste acid.

Two nitrators and one " pre-wash " tank usually constitute a factory unit, which is enclosed in a light wooden building and for safety surrounded with a high earthen embankment to localize the effects of an explosion. If it becomes necessary to " drown " a charge, the operators make good their escape as quickly as possible either through a tunnel in the embankment or by means of a bridge, according to their position or the design of the building.

Units in newer factories may have two nitrators, each with its own wash tank, in one building. The buildings are called nitroglycerine " hills ".

(*c*) *Washing.*

The nitroglycerine still contains much acid, which must be removed by washing. It is agitated with an excess of water by the injection of air into the " pre-wash " tank ; the air is then turned off and, on standing, the nitroglycerine forms a layer at the bottom. The wash water is skimmed off this layer by means of a funnel and rubber pipe device (J) which can be lowered by means of a flexible cord. The wash water flows away by the rubber pipe (L) to a " labyrinth ", a vessel divided into partitions by means of baffle plates ; any nitroglycerine carried over settles at the bottom of this and is eventually drawn off. From this the washings flow to a settling tank, where any final traces of nitroglycerine are allowed to settle out for recovery.

The washing process is repeated, three times in all with water, and thrice more with a dilute solution of sodium carbonate. The temperature in the washing tank can be observed by a thermometer (T) and fumes are drawn off by an exhaust pipe (M). The nitroglycerine is led away by the hose pipe (K).

In older plant the nitroglycerine now received a further series of about five washings in a tank similar to the " pre-wash " tank, situated in a separate washing house. The first washings were with dilute sodium carbonate solution and the last few with water. For these washings a temperature of about 30° C. was employed. In newer plant the washing is completed in the nitration house.

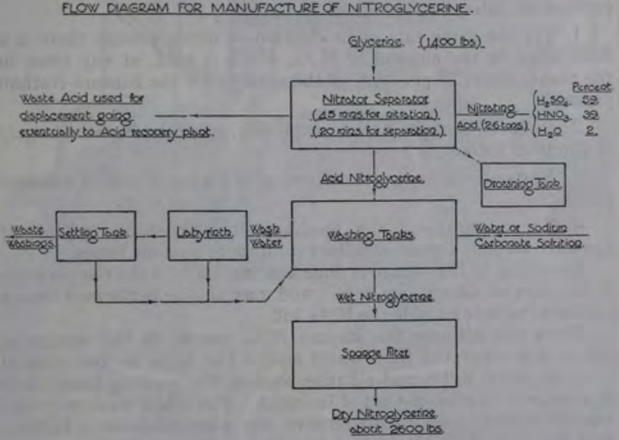


FIG. 12.2.

The nitroglycerine is now very slightly alkaline. It is finally run through a sponge filter to remove the last traces of water, is subjected to the heat test (*see* Chapter XVI) and is then ready for use, provided that the test is satisfactorily passed.

The yield is about 91 per cent. of that expected by theory, the above quantities giving about 1 ton of nitroglycerine.

The chemical reaction was illustrated in the introductory section. Fig. 12.2. shows the manufacturing processes in the form of a flow diagram.

II. Schmid Process

This process was evolved in Sweden and Austria after the Great War. There are now (1937) some dozen plants in the world, which work this process for making nitroglycerine.

In the Schmid process (as opposed to the Rintoul-Nathan process) the nitration is continuous, glycerine being run into the nitrator in a steady stream, while nitroglycerine with waste acid flows continuously from the top peripheral portion of the nitrator. The mixed acid flows in at the bottom of the nitrator and there mixes with the glycerine, which has already been partially nitrated by the waste acids of the nitrator.

The advantages of the Schmid process over the Rintoul-Nathan process are, inter alia, as follows :

1. For the same rate of production of nitroglycerine there is a diminution in the amount of N./G. which is held, at any time, in the plant (about 20 per cent. of the amount for the Rintoul-Nathan process).

2. Reduced sensitiveness to explosion, since the N./G. is largely in emulsion form.

3. Responsiveness to control, owing to the small bulk of material present.

4. The apparatus being mechanically stirred instead of air agitated, there is a much smaller evolution of noxious fumes.

Drowning of the charge is done automatically if the temperature in the nitrator rises above 28° C., and may also be performed from a separate traverse outside the N./G. hill.

From the nitrator the impure N./G. passes to the separator, where it is separated from waste acid. The N./G. is then treated with the usual water and alkaline washes, the washing being done in a series of towers instead of in tanks. The alkali wash may also contain sodium sulphite to remove any nitro-methane (CH_3NO_2) that may have been introduced as an impurity in the acid.

Properties and uses of nitroglycerine.

N./G. is a colourless oil of a specific gravity of 1·6, which is only very sparingly soluble in water, but is readily soluble in organic solvents (alcohol, acetone, etc.). N./G. is very poisonous, giving rise to violent headache (" N./G. head ") even by the absorption of minute quantities through the skin. Workers in factories, however, soon become inured to these effects and are no longer troubled by them. Cordite (which contains N./G.), if eaten, gives rise to a relapsing fever which resembles the " trench fever " of the Great War.

N./G. is slightly volatile, decomposes without boiling when heated and ignites at about 180° C., to burn quietly with a flame whose edges are tinged with green.

The use of N./G. is somewhat restricted by its sensitivity and

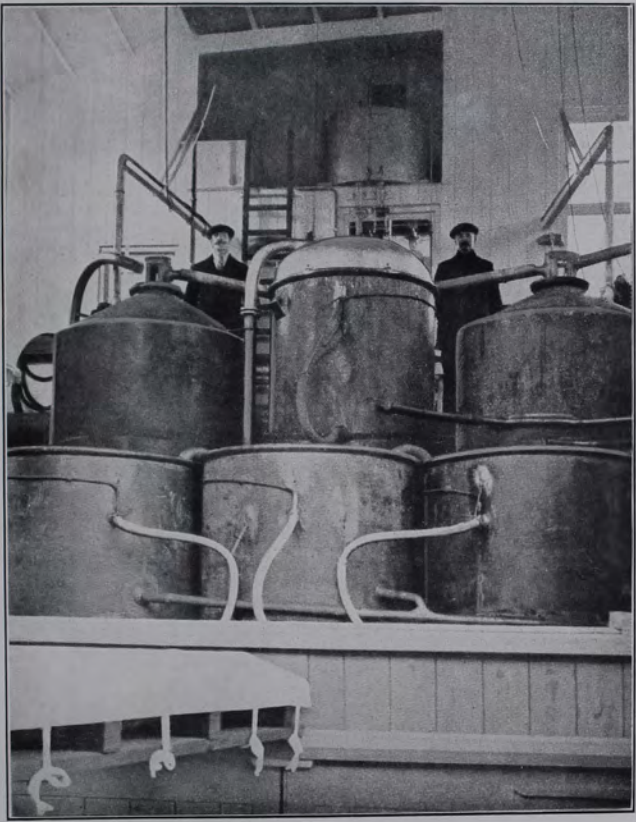


FIG. 12.3.—Interior of Nitrator House, showing Nitrator-Separator.

its liquid condition, although criminals use N./G. for opening safes, under the name of "soup."

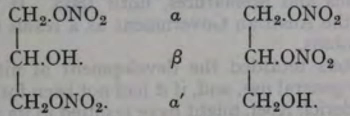
N./G. is gradually hydrolyzed by moisture in the presence of either an acid or an alkali. It possesses inherent instability, the acid products of its breakdown serving to accelerate its rate of decomposition unless they are freely allowed to escape or are neutralized by some stabilizer.

In the solid state N./G. can exist in two crystalline forms. The normal rhombic form melts at about 13° C. and is comparatively stable; while the triclinic form melts at about 2·8° C. and is much more sensitive. To the presence of the latter may probably be attributed many accidents which occurred during the thawing of dynamites in cold weather.

N./G. is a very powerful explosive with a maximum velocity of detonation of 8,000 metres per second, and is very sensitive to impact or friction. It is an important constituent of dynamite, blasting gelatine and gelignite; but by far its most important use in the service is for the manufacture of the cordite propellants. (For N./G. explosives, *see* Chapter XX. For cordites, *see* Chapter XV.)

Glyceryl Dinitrate

This occurs in two isomeric forms:

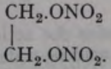


$$\begin{array}{lcl} CH_2.ONO_2 & \alpha & CH_2.ONO_2 \\ \quad | & & \quad | \\ CH.OH. & \beta & CH.ONO_2 \\ \quad | & & \quad | \\ CH_2ONO_2. & \alpha' & CH_2OH. \end{array}$$

Symmetrical or αα' *glyceryl dinitrate.* Unsymmetrical or αβ *glyceryl dinitrate.*

A mixture of these can be obtained by hydrolyzing glyceryl trinitrate by moderately concentrated sulphuric acid. This mixture is sometimes added to N./G. (for making dynamites, etc.) in order to depress the freezing point of the N./G. to prevent freezing in cold weather.

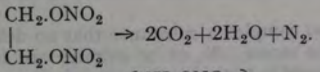
Glycol Dinitrate. (Dinitroglycol.)



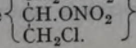
$$\begin{array}{l} CH_2.ONO_2 \\ | \\ CH_2.ONO_2. \end{array}$$

This is also used as an anti-freeze for N./G. It is made by nitrating ethylene glycol, $HO.CH_2.CH_2.OH$, a synthetic product, which is derived from ethyl alcohol, C_2H_5OH.

Dinitroglycol is a perfectly "balanced" explosive, which decomposes thus:



$$\begin{array}{l} CH_2.ONO_2 \\ | \\ CH_2.ONO_2 \end{array} \rightarrow 2CO_2+2H_2O+N_2.$$



Monochlorhydrin Dinitrate $\left\{\begin{array}{l} CH_2ONO_2 \\ CH.ONO_2 \\ CH_2Cl. \end{array}\right\}$ is also used as an anti-freeze for N./G.

CHAPTER XIII

NITROCELLULOSE, GUNCOTTON, SOLUBLE AND INSOLUBLE NITROCELLULOSE

Introduction.

The first record of nitrocellulose is in the investigation of the action of nitric acid on cotton by Pelouse in 1838. Some seven years later Schönbein discovered its value as a high explosive, and he also worked out a method for its preparation.

Under licence from Schönbein, its manufacture was started in this country at Faversham, but a disastrous explosion which occurred there in 1847 put a stop to it for some twenty years.

About 1852 von Lenk advocated the use of guncotton as a propellant for the Austrian artillery, and it was so utilized, in spite of many burst guns and prematures, until 1863. It use was then abandoned by the Austrian Government as a result of two serious magazine explosions.

These disasters retarded the development of nitrocellulose as an explosive for general use, and, if it had not been for the investigations of Sir Frederick Abel, might have resulted in its abandonment. He carried out a series of researches into the causes underlying the apparent instability of the explosive. This was found to be due to incomplete elimination of the residual nitrating acids, which set up rapid decomposition in the nitrocellulose. Abel showed that thorough purification after nitration was essential, and that it could best be accomplished by pulping the nitrocellulose, and then subjecting it to thorough treatment with both boiling and cold water.

Cellulose under the action of nitric acid (usually in conjunction with sulphuric acid as a dehydrating agent) forms the nitric esters which are commonly known as nitrocellulose. The term nitrocellulose is a misnomer, as the compounds formed by the action of nitric acid on cellulose are nitrates or nitric esters and no nitro-bodies. It would therefore be more accurate to refer to nitrocellulose as cellulose nitrate, but the older name has the authority of custom.

Cellulose is so complex a substance that no definite compounds corresponding to mono-, di- or tri-nitrates are formed. On the contrary, it is possible to prepare a series of nitrocelluloses in which the nitrogen content increases continuously from 6 per cent. to 14·14 per cent.

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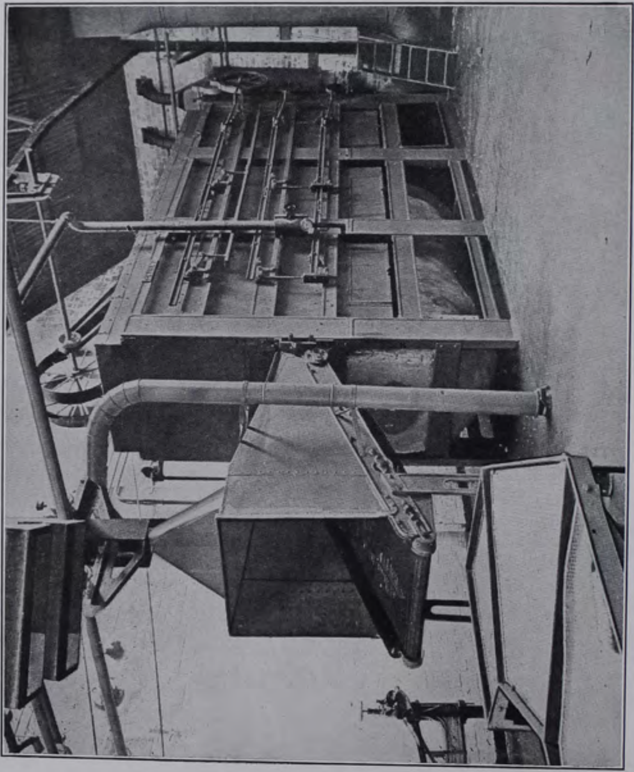

Fig. 13.3.—Cotton Drier.

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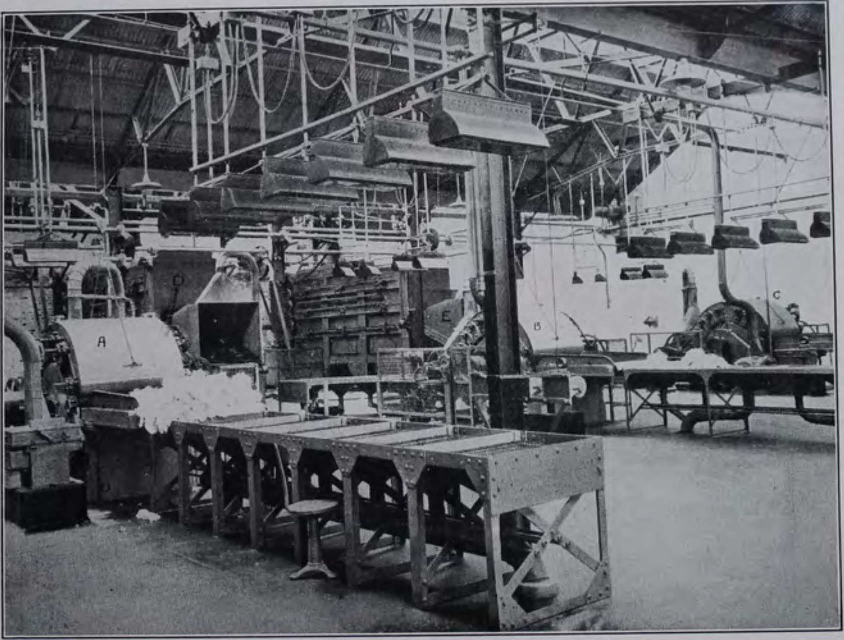

FIG. 13.2.—Machines for the Preliminary Treatment of Cotton Cellulose.
~~As used at Royal Naval Cordite Factory, Holton Heath.~~

FLOW DIAGRAM FOR THE MANUFACTURE OF "NITROCELLULOSE." FOR CORDITE M.D. OR GUNCOTTON.

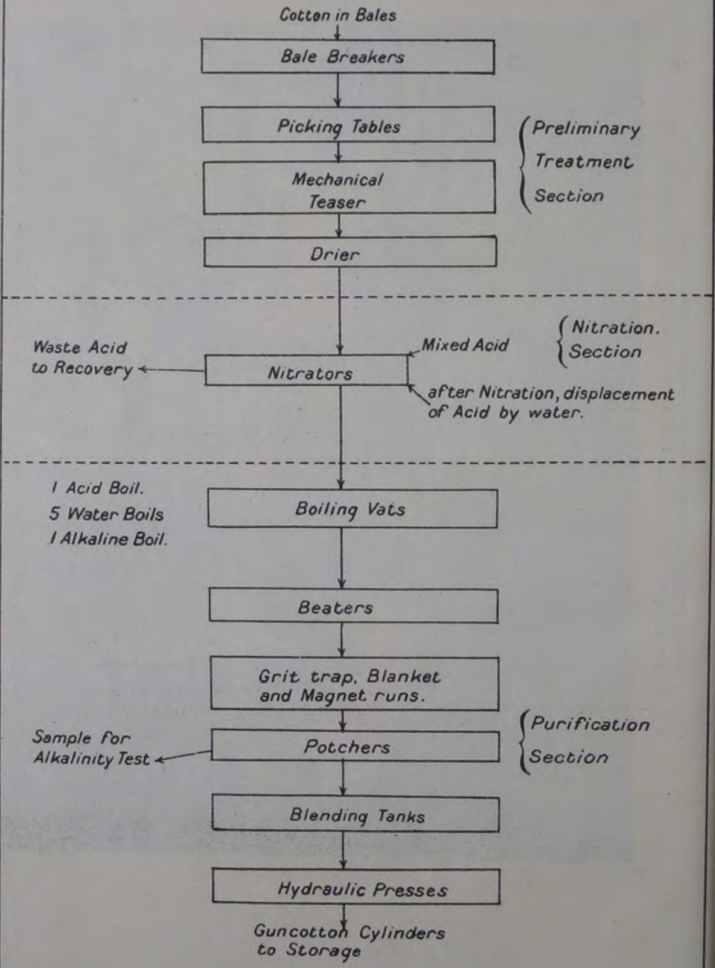

FIG. 13.1.

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Malby & Sons, Lith.

On explosion, or combustion, nitrocellulose yields entirely gaseous products, chiefly consisting of carbon monoxide and dioxide, water and oxides of nitrogen.

The Manufacture of Nitrocellulose.

The general reaction for the nitration of cellulose may be indicated by the equation :

$$C_6H_{10}O_5 + xHNO_3 \rightarrow C_6H_{(10-x)}O_{(5-x)}(NO_3)x + xH_2O$$

where x is not greater than 3.

The value of " x " varies according to the conditions of nitration, viz. (i) temperature, (ii) time of nitration, (iii) percentage of water present in the mixed acids. An increase in (i) and (iii) gives a lower, and an increase in (ii) a higher value to " x ".

In general, control is exercised through the medium of (iii). For example, the approximate compositions of the mixed acids for nitrocellulose, for use in the manufacture of cordite M.D. (13·1 per cent. N) and cordite R.D.B. (12·3 per cent. N) are as follows :

	W. or M.D.	*R.D.B.*
Sulphuric acid	70·0	62
Nitric acid	21·5	24
Water	8·5	14
	100·0	100

With this exception, the procedure and treatment is similar for all classes of nitrocellulose used for explosives.

A flow diagram for the method of nitration which is used at the Royal Gunpowder Factory, Waltham Abbey, will be found in Fig. 13.1.

The nitration of cotton cellulose is here considered.

1. *Preliminary treatment.*

(i) The cotton as received into the factory has passed the specification tests for acceptance. It arrives in bales, which have been hydraulically compressed.

(ii) The bales are opened, and partially broken up by hand, before the cotton is fed into the bale breakers.

These machines are generally arranged in sets of three, and the cotton is passed successively through each machine of a set, until it is thoroughly broken up. Three of these bale breakers are shown in Fig. 13.2, marked A, B, and C. In front of each machine is seen a table on to which the cotton emerges. These tables are strongly illuminated from above, and on them the cotton is spread out and subjected to a visual examination.

(iii) The cotton is then teased mechanically before it enters the drier (Fig. 13.3).

(iv) As received, the cotton contains some 8 per cent. of moisture. This must be reduced to less than 1 per cent. before nitration, or the heat produced by interaction between the sulphuric acid and the moisture would be great enough, in all probability, to ignite the mass. In the drying machine, the cotton is carried on to three shelves by a belt conveyer. The cotton traverses all three shelves before it emerges from the drier. The operation is quite continuous, but any one batch of cotton is in the drier for about 30 minutes. The temperature is maintained at 85°–90° C. by steam heating. Two driers (D and E) are visible in the background of Fig. 13.2. Below the letter D is the entrance to the drier, and the belt conveyer can be seen ascending towards the main compartment in the background. The rockers and bars operating the shelves can be seen to the left of the letter E.

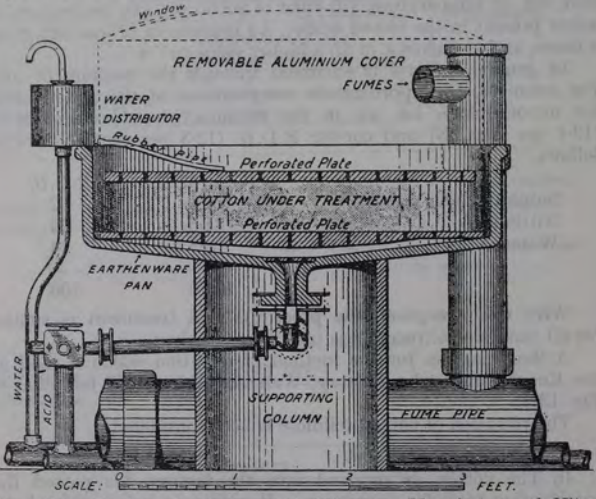

FIG. 13.4.—Section of Displacement Nitrator. (Manufacture of Nitrocellulose.)

From *Arms and Explosives.*

(v) The dried cotton is withdrawn from the drier by the suction of a large electric fan, through which the cotton passes on its way to large, glazed earthenware, storage bins.

(vi) From the bins, the cotton is weighed out into aluminium boxes, 26¼ lb. to a charge, and conveyed to the nitrators.

2. *Nitration.*

(i) Nitration is performed in stoneware Nathan and Thomson displacement pans (Fig. 13.4), which are arranged in sets, four pans to a set. The interior of a cotton nitration house is shown in

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FIG. 13.5.—Nitration House. (Manufacture of Nitrocellulose.)

Fig. 13.5. The set nearest the camera is shown in its complete state. The four pans constituting the set are numbered 1 to 4. The aluminium covers are fume hoods, and these are only placed in position during the operation of " dipping." The connection to the fume main can be seen at B. C is one of the stoneware nitrators.

The cotton is " dipped " in the mixed acid, which has been placed in the correct quantity in the nitrator. Stainless steel forks are used to push the cotton under the surface of the acid. When immersion is complete the cotton is covered over with stoneware slabs so as to keep it below the surface of the acid. Some of these slabs are visible in the photograph at A, A, A. To prevent fuming, water is gently run over the surface of these slabs when they are in position. Being lighter, it remains as a layer above the acid. The water inlet for four pans is shown at E in the figure.

Nitration to guncotton (13·1 per cent. N.) takes about 2½ hours, and the temperature of the acid supply is maintained at 17°–21° C. by coils containing cold refrigerator water in summer, and hot water or steam in winter.

(ii) After nitration is complete, cold water is run gently in at the top of the pan, while the spent acid is withdrawn from the bottom of the pan at the same rate. This displacement takes about three hours, the temperature being kept at about 8° C. by the use of cold refrigerator water.

(iii) The displaced acid is strong at the commencement of displacement and only requires the addition of a little fresh acid to render it suitable for further use. This strong acid is therefore conveyed by acid-main directly to the acid mixing plant.

As displacement proceeds, the acid becomes weaker, until at a pre-determined strength (indicated by the hydrometer in the sight box, which can be seen above D in the figure) it is diverted to an acid-main leading to the recovery plant. The hydrometer is automatic, a glass ball falling into a stainless steel ring and blocking the exit pipe when the specific gravity of the used acid falls below 1·1.

The two mains for strong and weak displacement acid can be seen at D. (Strong acid main nearest camera.)

The final portion of the displacement acid is too dilute to warrant recovery, and it is therefore run to waste.

The mixed acid supply is not shown, as the acid is fed into the nitrators from below, through a " star ", whence four pipes run, one to each of the nitrators.

3. *Purification.*

(i) The nitrocellulose is now removed to the boiling house. Here it undergoes seven " boils ", the water being changed after each boil. Wooden vats with a perforated false bottom are used; steam is admitted at the base, and serves both to heat and to stir the mass.

The acid remaining in the nitrocellulose after displacement is ample for the first boil which is intended to contain 0·1 per cent. acid and takes 12 hours. This is a most important step in the purification of nitrocellulose. During nitration, some of the cellulose is attacked by the sulphuric acid to form cellulose sulphates, which, being unstable products, would, if present in the nitrocellulose, break down, freeing sulphuric acid which accelerates the decomposition of the explosive. The 0·1 per cent. acid in this first boil is sufficient to hydrolyze these sulphuric esters.

Five " boils " with clean water follow, and they occupy 12, 4, 4, 4, and 4 hours respectively. Finally the nitrocellulose is boiled for two hours in water which is made alkaline, if necessary, by the addition of calcium carbonate, as it is imperative that all acid should be eliminated. The total time of boiling is thus $2\times12+4\times4+2=42$ hours.

(ii) An appreciable quantity of acid remains trapped in the fibres of the cellulose, and to remove this the nitrocellulose is pulped. Mixed with a large volume of water, it is conveyed from the boiling vats to beaters (Fig. 13.6) in which it is agitated for two hours between rapidly rotating knives. A battery of beaters is visible in the background of Fig. 13.7, numbered 1 to 6. The nitrocellulose leaves the beaters as a fine suspension in water.

(iii) From the previous operation, the notrocellulose flows along a trough fitted with vertical baffles. This trough acts as a grit trap, and from it, the nitrocellulose passes to a shallow trough, the bottom of which is covered with blanket cloth. The finer particles of grit and foreign matter are trapped by the blanket, and at the end of the " blanket run " the nitrocellulose passes over the poles of electric-magnets, which remove any particles of iron or steel which may have been picked up during manufacture. The " blanket runs " are visible in Fig. 13.7 at A, A, A.

(iv) By means of the gutter C, C, C (Fig. 13.7) the pulp runs into the " potchers " of which three are seen at B, B, B. Here, the nitrocellulose receives three final washings, being violently agitated with cold water for three periods of ten minutes.

Samples are taken and tested for alkalinity (which should be 0·2 to 0·4 per cent.), precipitated chalk being added if necessary.

At Waltham Abbey a new type of " swirl " potcher is being tried. This potcher is based on the principle that, when water runs out of a bath, a " swirl " is created. In this type of potcher, the swirling action is assisted by running water into the tank tangentially as shown in diagrammatic form in Fig. 13.8.

The potcher is lead lined and is about 8 feet deep and 8 feet in internal diameter. It has a capacity of about 8000 gallons.

(v) Blending is a simple operation. The nitrocellulose from all the nitrators is run into large tanks holding some 4 tons, and thoroughly mixed by stirring.

(vi) The blended nitrocellulose is then pressed into cylindrical

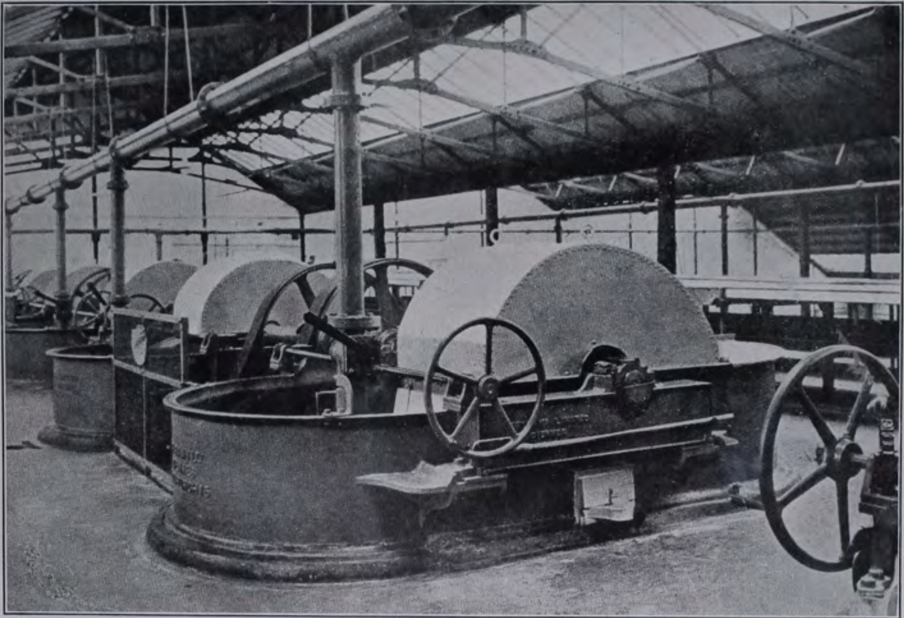

Fig. 13.6.—Beaters.

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FIG. 13.7.—Purification House. (Manufacture of Nitrocellulose.)

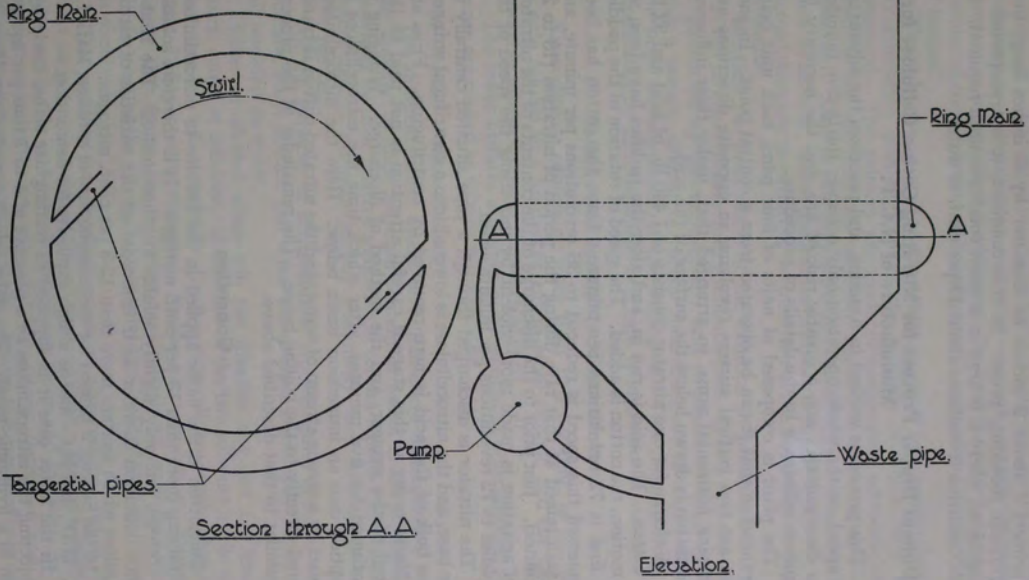


Fig. 13.8.
Principle of " swirl " type of potcher.

"primers" about 2 inches in diameter by 6 inches long, in a hydraulic moulding press. In this condition it is transported to magazines, where it is kept in a moist condition until required. In this condition it contains about 13 per cent. of water.

Dupont Dipper Process for Nitrating Cotton Cellulose for Manufacture of N.C.T.

This process is worked in America, and possesses the advantage of speed, as the whole operation only occupies thirty-five minutes. Its disadvantages are, a greater risk of fire, and the necessity for rigorous adherence to the details of procedure.

The plant is composed of units of four pans, each unit being arranged so that it can be operated from a central point. In each pan are two vertical stirrers revolving in opposite directions and carrying horizontal arms, so arranged that, under their influence, the cotton is drawn below the surface of the acid.

A charge for one nitrator consists of 1,440 lb. of acid and 32 lb. of cotton. The acid is run in, and after the paddles have been set in motion, the cotton is added. The speed of rotation of the paddles at first is 72 revolutions per minute. Once the cotton has been immersed this speed is reduced to 36 revolutions per minute, and is maintained at that rate during the period of nitration (18 to 24 minutes). Just prior to the discharge of the contents of the nitrator, the agitation is made more violent by increasing the speed of the paddles to 72 revolutions per minute again.

The nitrator is discharged through a pipe situated centrally in the base, and the nitrocellulose is lowered into a centrifugal wringer. The bulk of the acid is here removed by centrifuging. Fires are liable to occur at this stage if careful attention is not paid to the speed of the wringer, and the method of discharge. Wringing is continued for five minutes, after which time the nitrocellulose is emptied into an immersion basin below. Here the nitrocellulose is met by a strong stream of water, and the nitrated cotton is transferred directly to the boiling house. The remainder of the process is similar to that described above.

Guncotton

Guncotton is the name applied in the Service to nitrocellulose containing more than 13 per cent. nitrogen. It is therefore soluble in acetone, but only slightly soluble in ether-alcohol. The Home Office definition is wider as it embraces all the varieties of nitrocellulose which contain more than 12·3 per cent. nitrogen.

In the Service it is used for the manufacture of cordites, Mark I., W., M.D., and M.C., and as a high explosive for demolition.

In the latter case it is supplied in rectangular slabs, made by subjecting the nitrocellulose to a pressure of 4 to 7 tons per square inch in a hydraulic press. The slabs, which contain from 15 to 20 per cent. of water, are packed in sealed tin cases, and are periodically examined to ascertain that the water content has not decreased, more water being added if necessary. Sodium phenate $(C_6H_5O.N_a)$ is added to the nitrocellulose before pressing to prevent the formation of fungus.

The slabs are pierced in the centre in order to accommodate a dry guncotton primer, through the medium of which they are detonated. The primers are made of compressed nitrocellulose, dried in hot air until the moisture content is not greater than 1 per cent. After drying they are rendered waterproof by immersing them in acetone, which gelatinizes their surface. The primers are pierced centrally to permit of the insertion of the initiating fulminate detonator.

Mention has been made of the addition of precipitated chalk $(CaCO_3)$ to nitrocellulose during manufacture. It acts as a stabilizer in guncotton by neutralizing the acid products which, together with a certain amount of carbon monoxide, are liberated during the slow decomposition of the explosive. This decomposition is accelerated by direct sunlight and high temperature of storage.

Soluble and Insoluble Nitrocellulose

Nitrocellulose containing more than 12·8 per cent. of nitrogen is only soluble to a limited extent in ether-alcohol, and the name insoluble nitrocellulose is therefore applied to it.

The lower nitrates are completely soluble in ether-alcohol, and hence are classed as soluble nitrocellulose.

Properties of nitrocellulose.

The different nitric esters of cellulose are distinguished from one another by their nitrogen content, a useful index of which is provided by their relative solubility in certain liquids. The highest percentage of nitrogen in any commonly used nitrocellulose is 13·1 per cent.

All the varieties of nitrocellulose are soluble in acetone, amyl acetate, ethyl acetate and a few other organic solvents. They are all insoluble in water.

Ether or alcohol alone will not dissolve any but the lowest nitric esters of cellulose. A mixture of the two solvents in the proportions 3/2 will completely dissolve nitrocellulose containing less than 12·8 per cent. nitrogen. As the nitrogen content increases above that figure, the solubility rapidly falls off until only about 10 per cent. of the nitrocellulose containing 13·1 per cent. of nitrogen is dissolved.

The stability and insensitiveness of nitrocellulose (when dry) bear an inverse relation of the nitrogen content. The lower nitrates are very stable and very insensitive to blows and friction. As the nitrogen content rises, the stability slowly decreases and the explosive becomes more sensitive. Above 12·8 per cent. nitrogen, the stability and insensitiveness fall off with increasing rapidity until the compound approximating most closely to the trinitrate (14·14 per cent.) is very sensitive, and is so unstable that on formation it readily decomposes.

Nitrocellulose, when in a loose condition, is a cream-white friable mass. If dry, it ignites readily and burns fiercely, the products of combustion being entirely gaseous. The higher nitrates are sensitive to friction and blows, and can be readily detonated.

When wet, *i.e.* containing more than 13 per cent. water, it is one of the safest explosives in existence. It is insensitive to blows or friction, and cannot be ignited at once by a flame. It can only be detonated successfully by the detonation of a primer of dry guncotton, or similar initiator, in close contact with it. Wet guncotton is so insensitive that ordinary woodworking tools may be used on it provided they are kept wet.

Nitrocellulose which has been brought to the colloidal state by gelatinization with solvents, is a tough hard substance resembling horn.

Nitrocellulose is used in the Service in all propellants, of which it is one of the main constituents, since few of them contain less than 50 per cent. Its use as guncotton is extended to fillings for mines, etc.

CHAPTER XIV

SOLVENTS AND STABILIZERS.

SOLVENTS.

There are two solvents which are used in the manufacture of cordites : (i) acetone which is used for cordites made from insoluble N/C (*i.e.* Mk. I. M.D. and W), and

(ii) a mixture of ether and alcohol for gelatinizing soluble N/C as for cordite R.D.B. This mixture is commonly called ether/alcohol.

Acetone. (Dimethyl ketone $H_3C.CO.CH_3$).

There are three chief methods of preparing acetone :

(i) From calcium acetate.
(ii) By fermentation of vegetable matter.
(iii) From alcohol.

(i) *Acetone from calcium acetate.*

This takes place as represented by the following equation :

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow[380^\circ\text{ C.}]{\textit{Heat}} \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\text{Acetone}}{(CH_3)_2CO}$$

Calcium carbonate is made by treating lime with acetic acid, the latter being obtained either from the products of the destructive distillation of wood, or synthetically from acetylene (C_2H_2).

(ii) *Acetone from the fermentation of starch.*

Starch can be fermented to produce butyl alcohol and acetone. A fermentation process, using artichokes as the raw material, was worked out and operated at the Royal Naval Cordite Factory, Holton Heath, during the Great War, and yielded a mixture of butyl alcohol ($C_4H_9.OH$) and acetone.

(iii) *Acetone from alcohol.*

In this process, alcohol vapour and steam are passed over a suitable catalyst at 500° C. The resulting acetone is condensed.

$$\underset{\text{Alcohol}}{2C_2H_5OH+H_2O} \xrightarrow{500^\circ\text{ C.}} \underset{\text{Acetone}}{(CH_3)_2CO}+\underset{\text{Hydrogen}}{4H_2}+\underset{\text{Carbon-dioxide.}}{CO_2}$$

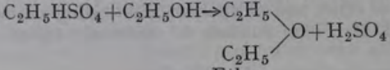
Acetone is a colourless volatile liquid of characteristic odour. It boils at 56° C. and has a specific gravity of 0·800 at 15° C. It is miscible with water in all proportions. Its importance in explosives lies in its ability to dissolve highly nitrated nitrocelluloses (over 13·0 per cent. nitrogen).

Ether-alcohol. The soluble nitrocelluloses (up to 13·0 per cent. nitrogen) are distinguished from those which are termed insoluble by their being dissolved in a mixture of ether and alcohol; maximum solvent power being obtained with a mixture of ether and alcohol in the proportion of 3 to 2.

(*a*) *Diethyl-ether* (*common " ether "*) $C_2H_5-O-C_2H_5$.

This substance is made by the action of sulphuric acid on ethyl alcohol.

(i) $$\underset{\text{Alcohol}}{C_2H_5OH}+H_2SO_4\rightarrow\underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5HSO_4}+H_2O$$

(ii) 

$$C_2H_5HSO_4+C_2H_5OH\rightarrow\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>O+H_2SO_4$$

Ether.

Crude ether results, together with a certain amount of alcohol, water and a little sulphur dioxide (SO_2). The ether is then purified by distillation.

More recently, a process has been introduced in which alcohol is dehydrated directly by passing the vapour over a heated solid catalyst:

$$2C_2H_5OH\rightarrow(C_2H_5)_2O+H_2O$$

Pure ether is a colourless, neutral, mobile and very volatile liquid which boils at 35° C. It has a well-known characteristic odour. Sp. gr. is 0·720/15° C. It is extremely inflammable, and great care is necessary for this reason. It is used as a solvent and has a large commercial outlet as an anæsthetic.

(*b*) " *Alcohol* " (*Ethyl alcohol, ethanol* $C_2H_5.OH$).

Alcohol is procured in the pure state by the distillation and subsequent drying of the crude spirit which results from the fermentation of many kinds of sugary or farinaceous vegetable matters, *e.g.* cane or grape sugar, barley, potatoes, etc. Wines and spirits contain alcohol, which is readily separated from them by distillation.

Alcohol is a colourless mobile liquid, with a vinous odour and a burning taste. It boils at 78·3° C. and burns with a pale non-luminous flame. With water, with which alcohol is miscible in all proportions, it forms a constant boiling mixture, which contains 4·41 per cent. of water. Alcohol is a useful organic solvent.

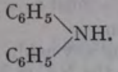
Stabilizers

(i) *Mineral jelly.* This substance is incorporated in Cordites Mk. I, M.D. M.C. and R.D.B. It was originally introduced into cordite, Mark I, as a lubricant, but was afterwards found to possess stabilizing properties. These have been traced to the presence of unsaturated hydrocarbons in the jelly.

By subjecting the jelly to a process of distillation known as "cracking", the percentage of these unsaturated bodies may be increased; this form of mineral jelly is known as "cracked mineral jelly" (C.M.J.) and is used in cordite M.C.

Mineral jelly is a mixture of petroleum hydrocarbons of high boiling point. It is made from the residue remaining after the distillation of American petroleum. For service purposes, limits are laid down, controlling the flash point, specific gravity, amount of foreign matter, volatile matter, and acidity.

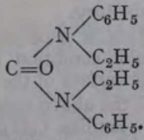
(ii) Diphenylamine



$$\begin{matrix} C_6H_5 \searrow \\ \quad NH. \\ C_6H_5 \nearrow \end{matrix}$$

This substance is used as a stabilizer in Ballistite and N.C.T. It is a crystalline substance, having a melting point of 54° C. and a boiling point of 302° C. It is insoluble in water, but is readily dissolved in alcohol and ether.

(iii) *Carbamite* (*or Centralite*) is symmetrical diphenyl diethyl urea.

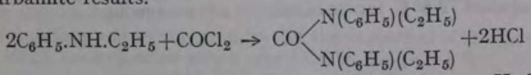


Aniline is first treated with ethyl alcohol in autoclaves at 165° C. This gives ethylaniline.

$$C_6H_5.NH_2+C_2H_5OH \rightarrow C_6H_5NH.C_2H_5+H_2O.$$

Aniline alcohol Ethylaniline.

The resulting ethylaniline is then treated with phosgene gas, and carbamite results.



$$2C_6H_5.NH.C_2H_5+COCl_2 \rightarrow CO\begin{matrix} \nearrow N(C_6H_5)(C_2H_5) \\ \searrow N(C_6H_5)(C_2H_5) \end{matrix} +2HCl$$

Phosgene Carbamite Hydrochloric acid.

Carbamite forms white crystals which melt at 72·5° C. when pure. It is used as a stabilizer, and to assist gelatinization, in solventless cordites and in Cordite W.

Several derivatives of urea ($CO(NH_2)_2$) have been suggested and used as stabilizers. The parent substance urea, readily absorbs the oxides of nitrogen which result from the decomposition of N/C and N/G, but is rather too strong a base to be used as a stabilizer for cordites. Carbamite, on the other hand, is a very weak base, owing to the presence of phenyl groups, and is very satisfactory as a stabilizer for cordites.

Methyl Centralite $CO[N(C_6H_5)(CH_3)]_2$ M.Pt. 121° C. is useful as a stabilizer and surface gelatinizer for N/C powders.

The action of, and choice of stabilizers.

These are substances which will combine with, and so render inactive, the decomposition products of cordite, which products would otherwise accelerate the further decomposition of the remaining cordite. It is clear that the stabilizer must not react with the cordite itself, although it must be so well incorporated with the other constituents of the cordite as to give a homogeneous colloid.

Stabilizers for N/C and/or N/G must :

(i) absorb oxides of nitrogen,
(ii) be capable of neutralizing any acid,
(iii) form a colloidal sol with the N/C or N/G,
(iv) be inert towards the N/C and N/G, as must also be the compounds which are formed by the union of the stabilizer with the decomposition products.

Of the above-mentioned stabilizers :

(*a*) *Mineral jelly* only fulfils conditions (i) and (iv) above. It is *not* therefore, very satisfactory.

(*b*) *Diphenylamine.* This is used extensively with N/C propellants. It does *not* fulfil condition (iii) above, and tends to accumulate in spots on the surface of the N/C.

(*c*) *Carbamite* fulfils all the above conditions. It is a very weak base, but gives some ethylaniline $C_6H_5NH.C_2H_5$ on combination with decomposition products. Ethylaniline, used alone as a stabilizer, would be too strong a base but is used up as it is formed from the carbamite.

(*d*) *Methyl centralite* may be of great use for, besides being a good stabilizer, it acts as a surface gelatinizer or " moderant " for N.C. propellants. In this connection, its high melting point (121° C. as against 72·5° C. for carbamite) is advantageous.

CHAPTER XV

CORDITES, N.C. PROPELLANTS. BALLISTITE

Table 15.A gives the composition and properties of various substances which have been used in the British service as propellants at one time or another.

Cordites

Introduction.

" Cordite " is the name applied in this country to a group of propellants which consist entirely of a uniform colloidal mixture of nitrocellulose and nitroglycerine, with the addition of a stabilizer. The propellant is usually employed in the form of sticks or cords (whence the name " cordite ") though this is by no means invariably the case.

Historically, cordite is a development of the smokeless powders, which were introduced about 1880. In 1882 the Explosives Company introduced their E.C. Powder, which consisted of " soluble " nitrocellulose, camphor, potassium nitrate, barium nitrate, and some colouring matter. The powder was partly gelatinized with ether/alcohol. These powders were excellent for smooth-bore weapons, such as shot guns, for which they are still made, but they were found to be altogether too rapid in burning for use in rifled firearms.

The French (Vielle 1884) partially overcame this difficulty with their Poudre B, which consisted of nitrocellulose gelatinized with ether/alcohol. The propellant was in the form of small squares cut from thin sheet.

This was followed in this country by the invention of Ballistite (Nobel 1888), an explosive which was used in the Great War, and which is described later in this Chapter.

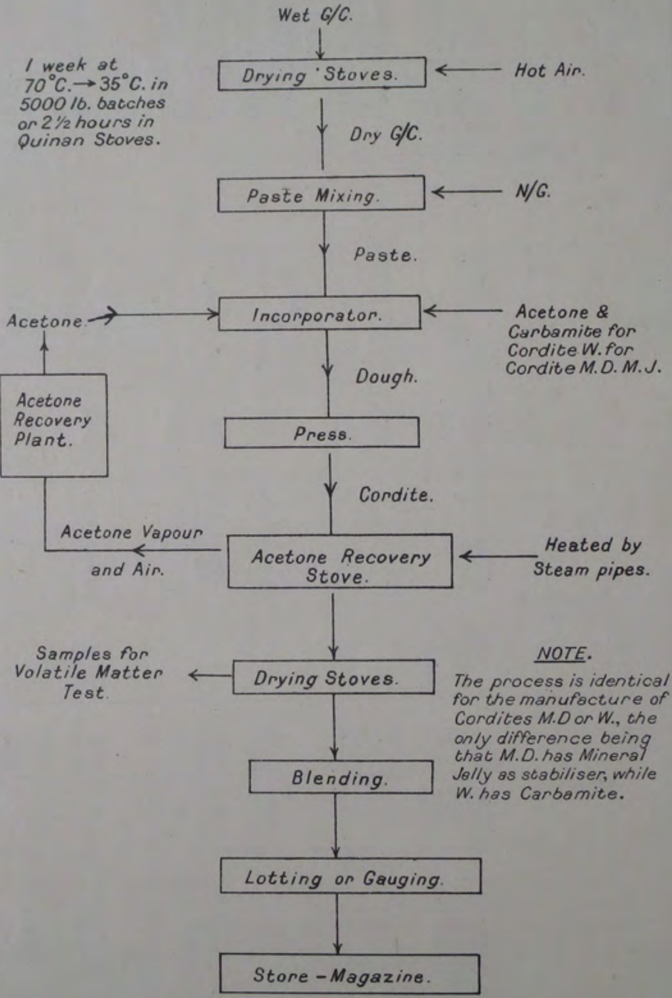
In the same year (1888) Cordite Mark I was recommended for use in the Service by a special committee, and was accordingly introduced in 1893

In the South African War, Cordite Mark I was found to be highly erosive, this being due to the high percentage of nitroglycerine (58 per cent.), which made this propellant very hot-burning, as a reference to Table 15.A will show. Cordite M.D. was, therefore, introduced. In Cordite M.D. a much lower percentage of nitroglycerine (30 per cent.) was employed. This has been most

TABLE 15.A. PROPELLANTS

PROPELLANT	Per cent. Composition			Nature of Stabilizer	Per cent. N. in N./C.	Physical Properties	Heat evolved cals./gram (water gaseous)	Vol. gas at N.T.P. c.c./gram.	Notes
	N./C.	N./G.	Stabilizer, etc.						
Cordite, Mark I	37	58	5	Mineral Jelly	13·1	Soft, easily marked by finger nail	1125	885	Very erosive
Cordite M.D.	65	30	5	Mineral Jelly	12·9 to 13·2	Hard, smooth	940	935	Less erosive, less N./G. Therefore more propellant needed
,, M.C.	65	30	5	"Cracked M.J.		Horny, brittle			
,, R.D.B.	52	42	6	Mineral Jelly	12·2	Rough, not brittle. Between Mark I and M.D.	914	960	More N./G. compensated by low N. in N./C. and more M.J.
,, W.	65	29	6	Carbamite	13·1	Like M.D.	945	935	As for M.D.
,, S.C.	50	41	9	Carbamite	12·2	Smooth, rather brittle	900	940	As for R.D.B.
Ballistite	60	40	—	—	12·6	—	1135	830	Erosive
N.C.T.	99·5	—	0·5	Diphenylamine	13·0 made up of 35 per cent. of 12·6, 65 per cent. of of 13·2	Hard. Hygroscopic	780	960	—
N.C.Z.	93	—	0·6	*Diphenylamine		—	815	930	—
Gunpowder	—	—	—	—	—	Hygroscopic, unless coated with graphite	726	256	56 per cent. of solid residue

FLOW DIAGRAM FOR MANUFACTURE OF CORDITES M.D. AND W.



NOTE.

The process is identical for the manufacture of Cordites M.D or W., the only difference being that M.D. has Mineral Jelly as stabiliser, while W. has Carbamite.

FIG. 15.1.

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successful in increasing the life of guns, and is still one of the chief propellants in use in the Service. For later developments as regards Cordites R.D.B., W., and solventless cordites *see* Chapter III and the end of this Chapter.

The manufacture of Cordites M.D. and W., is considered in detail in this Chapter; for other cordites, the manufacture is only described in so far as it differs from that of Cordites W. and M.D.

Cordite is a colloidal mixture of nitrocellulose and nitroglycerine, and contains enough oxygen to ensure that the products of combustion are gaseous. These products of combustion are colourless; it is true that dense clouds of reddish-brown fumes are formed when large guns are fired, but this is an after effect.

Note.—The process is identical for the manufacture of Cordites M.D. or W., the only difference being that M.D. has Mineral Jelly as stabilizer, while W. has Carbamite.

When combustion takes place inside the gun, nitric oxide (NO) is one of the gases formed; when this comes in contact with the outer air it is oxidized to nitrogen peroxide (NO_2), which is the reddish-brown gas to which reference has been made.

The Manufacture of Cordites M.D. and W.

"W" stands for Waltham Abbey, where Cordite W was developed.

Fig. 15.1 gives a flow diagram of the processes.

1. *Drying of the Nitrocellulose.*

The nitrocellulose as received into the cordite plant contains, for safety, some 30 per cent. moisture. The nitrocellulose is in the form of compressed cylinders. These are dried in stoves by hot air. The cylinders are stacked on racks of galvanized iron wire supported on wooden frames. The nitrocellulose is liable to become electrically charged in drying, and therefore, to avoid any danger from sparking, each rack is "earthed".

Drying takes 60 hours, the inlet temperature of the hot air varying from 70° C. at the commencement of the period, down to 35° C. at the end. In this type of stove, the nitrocellulose is dried in 5,000-lb. batches.

Quinan Stoves.

In this type of stove, the guncotton is dried in portions of about 25 lb. each, 15 such portions being dried in each Quinan Stove. There is, therefore, never more than about 300 lb. of dry guncotton in a Quinan Stove at any one time.

The advantages of the Quinan Stove over the first-mentioned type of stove are:

(*a*) A Quinan stove never contains more than 300 lb. of *dry* guncotton as against about 3,500 lb. in the other type of stove.

In the event of an explosion or fire, therefore, the effect is more likely to be localized.

(*b*) Quinan Stoves cut down the time of drying of the guncotton from 60 hours to less than 12 hours.

Each Quinan Stove has 15 drying tables. Hot air is passed in from below, and passes through a horizontal wire gauze on top of the table. Over this gauze is stretched a cloth, on which is placed about 25 lb. of wet guncotton from the nitration house. When the chargeman considers the guncotton to be dry, judging by touch, a determination of volatile matter is made. If the guncotton contains over 1 per cent. of water, it needs more drying. In practice, the operation of drying reduces the moisture content of the guncotton down to 1·0±0·4 per cent. When the guncotton is dry, the whole portion is bundled up in the cloth and removed.

2. *Paste Mixing.*

The " dry " nitrocellulose is now ready to be mixed with nitroglycerine. It is transferred to the paste-mixing house in waterproof canvas bags, each bag containing a charge of 39 lb. of dry N./C. on the basis of 60 lb. of finished cordite (dry basis). This charge, after the addition of 18 lb. of nitroglycerine, which is measured in from a burette, is emptied on to the mixing table (Fig. 15.2) ; a lead trough having a depression at one end. The mixture is worked by hand, on the table, and through a sieve of half-inch holes at the bottom of the depression into a bag attached below. The product is known as " paste."

am

3. *Incorporation.*

The " paste " is conveyed to the Incorporation house on canvas-covered aluminium bogies. The incorporator (Fig. 15.3) is similar to the dough mixer of a machine baker. It consists of a rectangular trough containing two shafts each fitted with four blades which rotate in opposite directions, one shaft at about 40 r.p.m. and the other at twice that rate.

A charge of " paste " is loaded into the incorporator and during loading a measured quantity of acetone (97 per cent. strength) is slowly added. For M.D. Cordite the machine is run for 3 hours ; at the end of that period the appropriate quantity of mineral jelly is added. Incorporation is then continued for another 3 hours, when the " dough ", as it is now called, is ready for the next process.

For cordite W, the carbamite is added at the beginning of the operation and the incorporation is continued for 6 hours.

4. *Pressing.* In this operation the " dough " is pressed, through a die, emerging in the familiar cord form of cordite. This is accomplished in a hydraulic press (Fig. 15.4), in which the dough is forced in one operation through a series of muslin and wire gauze strainers and finally through a die containing holes of the diameter requisite to give the desired size of cord.

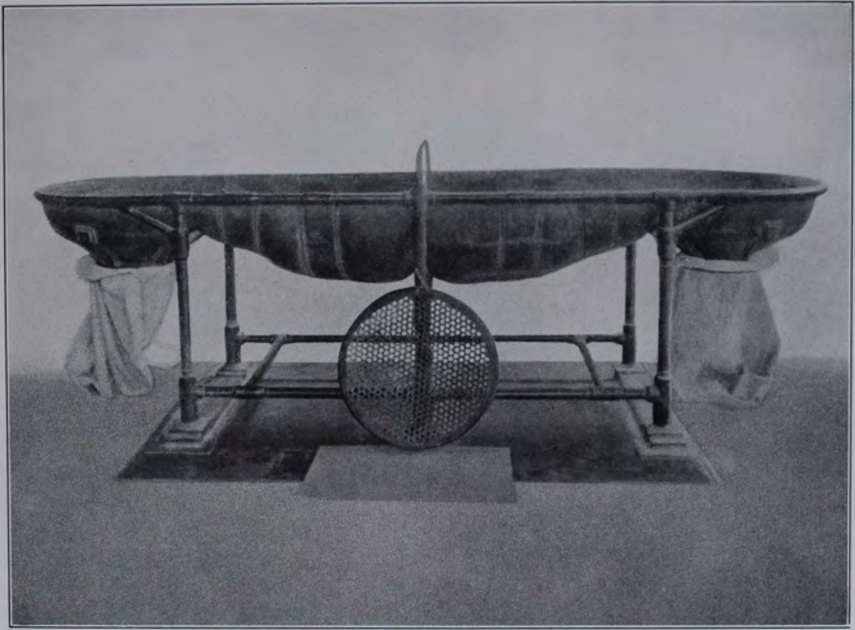

FIG. 15.2.—Cordite Paste Mixing Trough.

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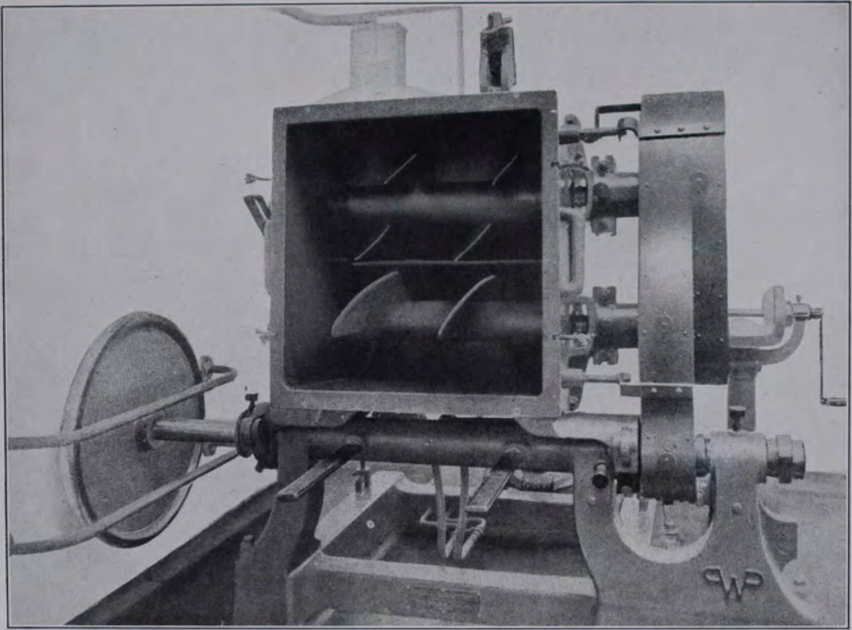

FIG. 15.3.—Incorporator. (Cordite Manufacture.) In tilted-up position.

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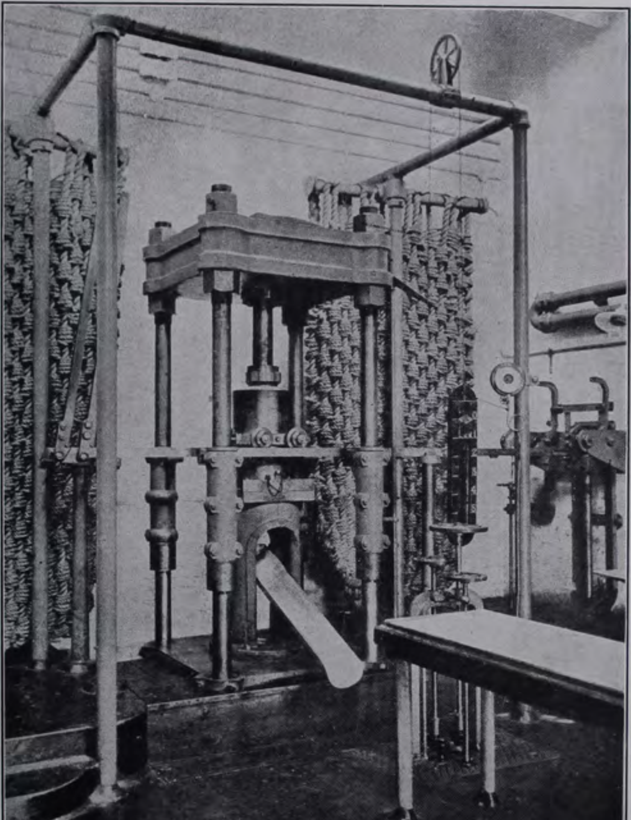

FIG. 15.4.—Cordite Press.

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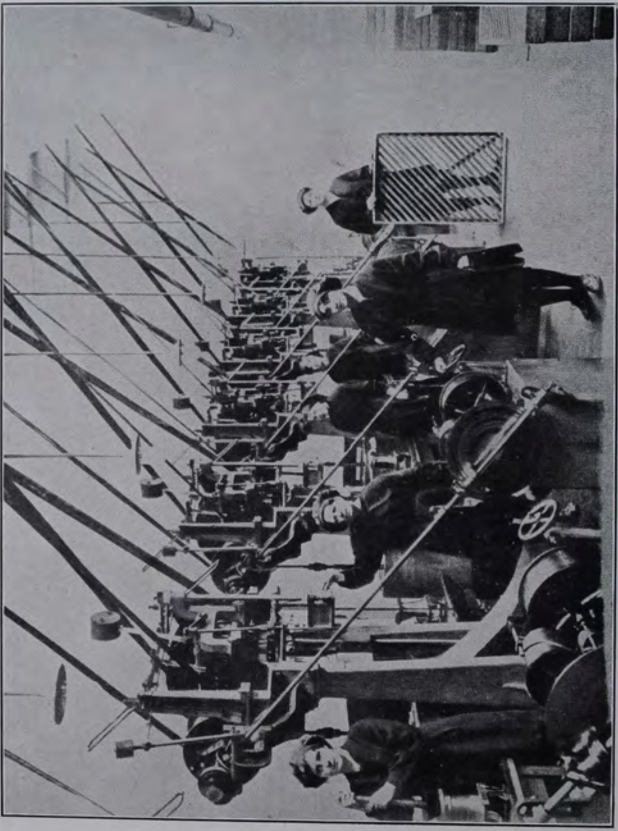


Fig. 15.5.—Rifle Cordite Presses.

5. *Cutting or reeling.*

(*a*) In the case of the larger sizes, the cordite, as it leaves the press, is collected by hand and cut off into measured lengths. The lengths are those for the final cartridges plus an allowance for shrinkage.

(*b*) In the case of the smaller sizes (*e.g.* rifle cordite) a die with a single orifice is used. As it is extruded, the cordite is wound on to small reels each carrying about a mile of cordite. The reels are then conveyed to the solvent recovery and drying stoves.

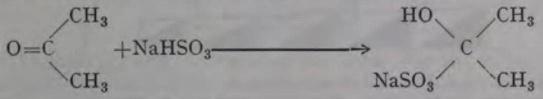
6. *Acetone recovery.*

The cordite is conveyed to the acetone recovery stoves on shallow wooden trays, which are stacked in chambers heated by steam pipes. Each chamber, as it is filled, is sealed, with the exception of a small opening at the bottom of the door.

Stoving occupies a week, the temperature being maintained at not more than 43° C. during that time.

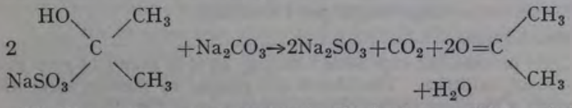
The acetone vapour, mixed with a large excess of air, is drawn by suction from the stoves to the adjacent recovery plant.

(i) The vapour there passes through a series of towers, counter-current to a stream of sodium bisulphite solution (15–30 per cent.). The acetone combines with the bisulphite to form a soluble salt :



Acetone. *Sodium Bisulphite.* *Acetone Sodium Bisulphite.*

(ii) From this salt the acetone is recovered by distillation with a solution of sodium carbonate :



(iii) The acetone so recovered is obtained as a dilute solution in water. This solution is liable to be slightly acid and, if this is so, caustic soda (NaOH) is added until the whole is neutral.

(iv) A final distillation procures the acetone in a concentrated form suitable for further use. About 50 per cent. of the acetone can be recovered under normal working conditions.

7. *Stove drying.*

The cordite is removed to the final drying stoves, which are similar to those used in the previous operation. No attempt is made to recover any of the solvent that may be driven off at this stage, as the vapour is too dilute to render such recovery economical.

The temperature of the drying stoves is maintained at about 40° C. The time of drying varies with the size of the cordite.

Thus, for Cordite M.D.:

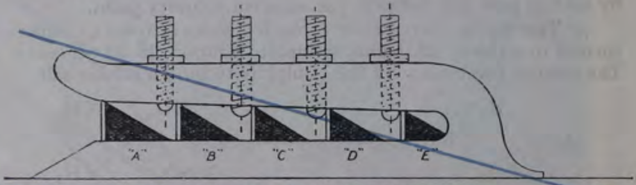
Size 45 requires 37 days.
,, 19 ,, 14 ,,
,, 4¼ ,, 7 ,,

The drying times are somewhat less than the above for corresponding sizes of Cordite W.

Towards the end of the drying period samples are taken for the specification test for volatile matter.

8. *Stove blending.*

Each operator engaged in unloading a stove mixes the contents of ten trays of cordite into a case. The cases are numbered, and about 30 cases constitute a "blend"; the blends are also numbered. 100 sticks are taken from each blend as a sample for the average weight per 100 inches.



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~~Fig. 15.6.—Machine for Gauging Cordite.~~

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9~~A~~. *Lotting.*

Blends are further mixed into lots, eight blends forming a lot. These lots are so mixed that a sample of 100 sticks from any lot is of the correct average weight per 100 inches.

~~9B. *Gauging.*~~

This process has superseded lotting, as it is found to give more consistent ballistics. The blends are gauged by passing each stick through a machine shown diagrammatically in Fig. 15.6.

At present this is a manual operation, but could be replaced by machinery.

The gauge consists of a brass guide, along which a stick of cordite may be moved. Four brass micrometers are mounted as shown in the figure, each being set for a slightly different diameter of cord, decreasing progressively from left to right. The operator slides a stick between the jaws of the gauge, and along until the stick meets a micrometer which will not allow it to pass. The gauge is thus a simple "GO" and "NOT GO" gauge. If the stick fouls the first micrometer, the operator pushes the stick forward until it falls into a chute guiding it to a box marked "A".

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~~Similarly a stick failing to pass the second micrometer, falls into a box marked " B " ; and so on. Sticks passing all the micrometers are collected in a box marked " E ". Sticks of the correct size are confined to box " C ".~~

~~At present size " A " (very large) and size " E " (very small) are discarded and the cordite is sent back to be re-worked. Equal amounts of sizes " B " and " D " are blended with size " C ", the resultant lot having an average diameter of cord " C ".~~ Deleted am 1

10. *Packing and storing.*

Finally, the cordite is placed in store to await the result of the acceptance tests ; it is then packed and is ready for despatch to the filling factories.

11. Reference has been made to rifle cordite, which is collected on reels after pressing, and is retained on these reels during the two stoving operations. Blending is carried out by winding the contents of several of these reels simultaneously on to one large drum ; these drums are sent to the filling factories after the usual tests.

The above description of the manufacture of Cordites M.D. and W. applied also to the manufacture of Cordites Mark I and M.C. Cordite R.D.B. and the " solventless " cordites are treated somewhat differently. Cordite M.D. is now only made for rifle sizes ; Cordite W. being made for cannon sizes.

Cordite R.D.B.

The shortage of acetone during the Great War led to the introduction of Cordite R.D.B. A reference to Table 15.A (p. 100) shows that Cordite R.D.B. differs from the other cordites in the employment of nitrocellulose containing only 12·2 per cent. nitrogen. This is a " soluble " nitrocellulose, and ether/alcohol, therefore, may be used as a solvent instead of acetone.

Its manufacture is very similar to that of Cordite M.D., with certain important exceptions, which are considered in detail below.

1. In the incorporator, ether and a certain amount of additional alcohol (if necessary) are added in place of acetone, the mineral jelly being introduced as before.

2. *Solvent recovery.* The solvents are evaporated in a stove and the vapours collected and absorbed in cresol, from which they are subsequently recovered by distillation. At the explosives works at Gretna, during the Great War, 36 per cent. of the ether and 83 per cent. of the alcohol used were recovered in this way.

3. The final stove drying is much quicker than for M.D. For example, size 60 Cordite M.D. requires 77 days at 45° C., as against 44 days at 45° C., for the same size of Cordite R.D.B.

" Solventless " Cordites.

The use of volatile solvents (*e.g.* acetone and ether/alcohol) in cordite manufacture entails serious disadvantages. These solvents must either be imported, or made in this country, in which case their manufacture necessitates the use of foodstuffs as raw material ; a factor which is to be deprecated in time of war.

In addition to these drawbacks, their use is attended by technical disadvantages. Recovery and drying stoves are necessary : these are expensive to erect, costly to maintain, and cover a large acreage. During the processes of recovery and drying much time is occupied, and many weeks' supply of cordite is thereby held up ; a serious matter in an emergency.

The stoving operations also react disadvantageously on the propellant, introducing irregularities in the cordite consequent on the shrinkage which occurs during the evaporation of the solvent. The " life " of M.D. cordite is also appreciably affected by its maintenance at a comparatively high temperature (about 110° F.) for several days.

To overcome these difficulties, the " solventless " process was designed for Naval cordite. The principles employed are not very different from those underlying the manufacture of ballistite. That is to say, the gelatinization of the nitrocellulose is mainly carried out by the nitroglycerine, but, to admit of the use of higher proportions of nitrocellulose than would be possible by this means alone, a substance is added, which, while acting as a stabilizer in the finished propellant, serves during manufacture to enhance the gelatinizing action of the nitroglycerine. A brief mention of some of these stabilizers will be found in Chapter XIV.

The name " solventless " cordite is, therefore, somewhat misleading ; the characteristic feature of these propellants being the employment of a non-volatile solvent.

The time occupied in manufacture is very much less than in the case of the production of other forms of cordite. It is, however, not quite so safe to manufacture, as the extremely viscous nature of the sheet cordite necessitates the use of high temperatures and heavy pressures for extrusion. Particular attention has to be paid to the provision of screens, so that the workers are adequately protected. As an offset to this disadvantage, the entire absence of loose, dry nitrocellulose must be noted.

Advantages of the " solventless " cordites.

Some of these have been mentioned, but it may be useful to recapitulate.

1. Increased " life " of the propellant, and increased output in a given time are a result of the absence of the stoving operations, which of necessity attend the use of a volatile solvent.

2. Initial expense and cost of maintenance are reduced, since the plant required for the manufacture of these cordites is much smaller than is necessary for the production of the other types.

3. The absence of the stoving and drying processes eliminates the possibility of shrinkage and distortion of the finished cordite.

"Solventless" cordite is very uniform in its dimensions, which conduces to regular ballistics.

4. In use, it is a cool-burning propellant, and its general properties are not unlike those of cordite M.D.

Disadvantage. A disadvantage of "solventless" cordite is the impossibility of straining it during pressing. It is difficult, therefore, to avoid the inclusion of small particles of foreign matter, but this disadvantage is more than outweighed by the higher degree of stability which is conferred by the stabilizing effect of carbamite.

Properties of Cordite.

Cordite is a "colloid", *i.e.* it has no internal structural form (*see* Appendix III). For this reason it burns comparatively slowly. The hot gases being unable to penetrate into the interior of the sticks, burning takes place layer by layer. Control, therefore, of the rate of burning can readily be exercised by varying the size or form of "cord".

It is a translucent substance, varying in colour from golden-brown to dark brown.

When in good condition it has little smell. When decomposition is advanced a distinct sour smell (due to nitrogen peroxide) is discernible. In the case of the "solventless" cordites, the characteristic odour of carbamite is sometimes apparent.

Finely ground cordites ignite in the range 150°–160° C. Ignited in the open in small quantities, cordite burns fiercely, but a small degree of confinement is quite sufficient to accelerate the rate of combustion to the degree of explosion. The combustion of cordite of small diameter can be brought to a very high order of explosive violence, and it can be detonated if suitably initiated.

Cordite is poisonous owing to its content of nitrogylcerine. Direct sunlight will cause some deterioration, and for this reason cordite should always be covered as much as possible. It is somewhat difficult to ignite, and the use of a gunpowder or guncotton igniter is therefore necessary.

Backflash. About 50 per cent. of the gases produced on ignition and explosion of cordite in a gun are inflammable, and ignite on contact with the outside air. This may be a source of danger in big guns, especially if the breach is enclosed in a turret. For this reason these gases are expelled, in the case of the largest weapons, by a compressed air blast.

Further, even if ignition of the gases does not take place, they are dangerous, as carbon monoxide is one of the chief products of the combustion of cordite. This, of course, is exceedingly poisonous, and cases have occurred of gun crews in turrets being overcome by it.

"Sweating". This term as applied to cordite has two distinct applications.

(*a*) At low temperatures, nitroglycerine is exuded. This may take place at and below 32° F. for M.D., W. and M.C., or 45° F. for Mark I and R.D.B. Prolonged storage under these conditions may affect the ballistics, and there may be a discordance in some of the tests applied to cordite, due to the loss of nitroglycerine. Chemical decomposition of cordite at very low storage temperatures is very slow, and advantage might be taken of this to increase the life of cordite if the separation of nitroglycerine could be avoided.

The presence of exuded nitroglycerine may be detected by wiping a stick of the cordite with a piece of blotting paper. If this be then ignited, any nitroglycerine absorbed by the paper will be evidenced by the accelerated combustion and by the appearance of a greenish tinge at the edge of the flame (R.A.O.S. II, Pamphlet 7).

(*b*) At temperatures exceeding 80° F., mineral jelly may be exuded.

Stability. Cordite is *not* a thoroughly stable substance ; a slow but continuous decomposition goes on, resulting in the formation of free nitric and nitrous acids. The action is accelerated by external heat. The internal heat generated by the chemical action of decomposition is not carried away rapidly, since cordite is a bad conductor, having a thermal conductivity about equal to that of porcelain. To retard the rate of decomposition of cordite, substances (stabilizers) are added to it, which combine with the free acids to form innocuous products, and so stabilizes the propellant.

If decomposition proceeds far enough sufficient heat may be generated to ignite the cordite. To guard against this, periodical tests are carried out. These tests are described in detail in R.A.O.S. Part II, and outlined in Chapter XVI. The amount of decomposition is small and does not suffice to affect ballistics.

The temperature of storage has a great effect on the " life " of cordite, and it should not be allowed to exceed 70° F. if possible.

Contact with iron or wood affects the stability of cordite owing to chemical action being set up. Non-absorbent paper is therefore used to line all cordite boxes.

Nitrocellulose Tubular (N.C.T.)

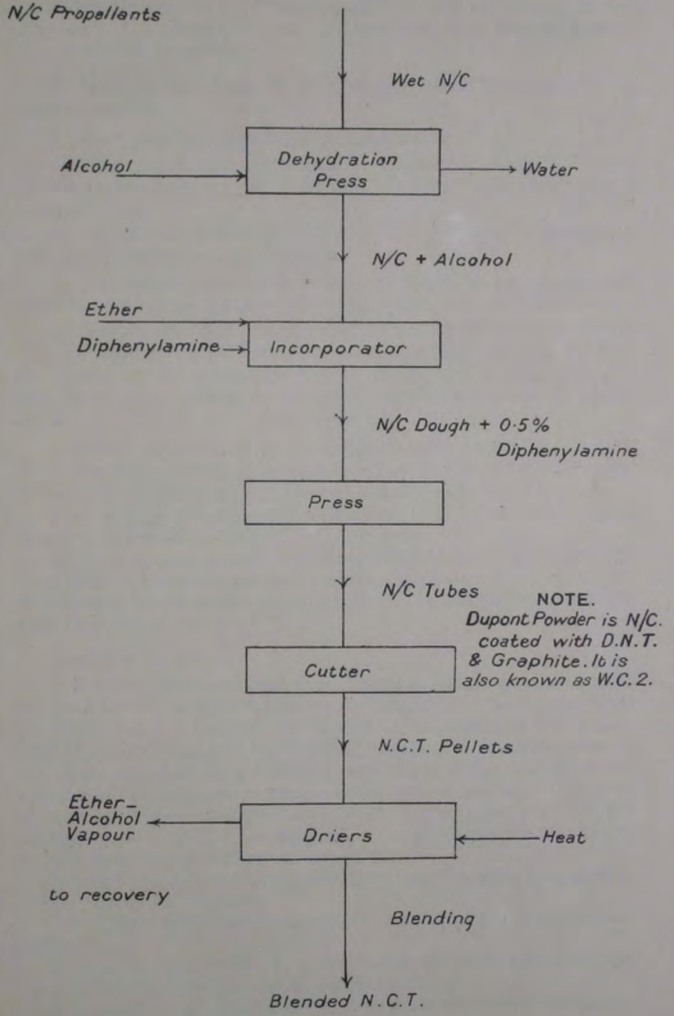
This is the standard propellant in the U.S.A., and large quantities were imported thence for use in the service during the Great War. Its manufacture was also developed to a small extent in this country.

Fig. 15.7 is a flow-diagram showing details of the process of manufacture. The operations are similar to those of R.D.B. Cordite, with the following exceptions :—

1. No nitroglycerine is used, and thus there is no paste mixing. Alcohol dehydration of the N./C. is employed.

2. 0·5 per cent. of diphenylamine is used as a stabilizer in two of the varieties of N.C.T., viz. that which was manufactured in Great Britain and that made by the Dupont Company in the U.S.A.

FLOW DIAGRAM FOR MANUFACTURE OF N.C.T.



NOTE.
Dupont Powder is N/C. coated with D.N.T. & Graphite. It is also known as W.C. 2.

N/C. = Nitrocellulose.
D.N.T. = Dinitrotoluene.

FIG. 15.7.

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Dinitrotoluene is used to regulate the rate of burning of the Dupont N.C.T. used in S.A.A. In addition, this Dupont powder is coated with graphite.

3. Incorporation takes 45 minutes as opposed to 6 hours in the case of cordites.

4. Four pressing operations are required.

(*a*) The dough as removed from the incorporator is a very friable mass, and must be compressed in order to make it into a compact form.

(*b*) The nitrocellulose is then filtered by forcing it through a wire gauze strainer under pressure.

(*c*) The altering operation breaks up the N./C. once more, and a further compression is needed to regain the compact condition.

(*d*) Finally, the N./C. is extruded through a die under pressure. The die forms a cord with seven holes running longitudinally through it. Owing to the extremely viscous nature of the dough, the die has to be water cooled to keep its temperature down to about 35° C.

5. N.C.T. is not used in the form of cord, as it is too brittle. It is therefore cut into short cylinders having a length about equal to twice their diameter, and pierced longitudinally with 7 holes.

Final drying takes a considerable time in the case of the largest sizes ; 4 to 5 months at 44° C. is quite usual.

N.C.T. is known in its various sizes by its diameter in hundredths of an inch. The sizes employed in this country were 5, 11, 16 and 22. It was used for all natures of howitzer, but it was not employed for guns larger than the 60-pr.

Properties of N.C.T.

N.C.T. is lighter in colour than, and it is not so well gelatinized as, cordite. It is also hygroscopic, and absorbs moisture. This moisture does not prevent functioning as an explosive, but causes variations in ballistics ; thus giving inaccurate shooting, due to the heat absorbed in volatilizing and dissociating the absorbed water, with its consequent effect on the rate of burning. The ease of ignition is also affected, particularly if the powder grains are externally wet. N.C.T. is also liable to alteration in density on storage, due to loss of residual solvents.

It is not so stable in storage as cordite, and it is therefore unsuitable for use in hot climates.

The fumes from the explosion of N.C.T. under pressure are poisonous.

A disadvantage of N.C.T. is, that it is so much less powerful than cordite that the charges are rather bulky.

It possesses the advantage of burning more slowly and more uniformly than cordite, and it causes less erosion.

Ballistite.

Introduction.

This explosive, which was invented by Nobel in 1888, was the forerunner of Cordite Mark I. It differs from that propellant in two respects: (i) "Soluble" nitrocellulose is used, and (ii) the N./C. is gelatinized by nitroglycerine, and not by a volatile solvent.

Ballistite has the following composition:

	Per cent.
Nitroglycerine	39·5
Nitrocellulose (12·6 per cent. N.)	60·5

Manufacture. Fig. 15.8 is a flow-diagram of the process.

1. The N./C., in the form of a wet pulp, is agitated with the correct amount of N./G. by compressed air, in the presence of a large excess of water. The N./G. is absorbed by the N./C., and the majority of the water can then be removed by draining.

2. After pressing, the water content is reduced to about 2 per cent. by passing the mixed N./G. and N./C. between hot rollers. The dry, ungelatinized, mixture is then incorporated by passing it between rollers which are internally heated by steam, so that rolling is carried out at about 60° C. The explosive emerges as a thin sheet, which is folded over and passed again through the rollers. This operation is repeated several times, until a uniform gelatinous material is produced (Fig. 15.9).

3. The propellant is then cut into flakes, 4 mm. square by 0·71 mm. thick, after which it is blended.

During the Great War the process was modified, in order to accelerate the rate of production. After wet mixing and pressing, the mixture was partially gelatinized with acetone/alcohol (70/30). The remainder of the process was as described above.

Properties.

Ballistite is a dark-brown translucent material, which has the appearance of being well gelatinized. In the service it is always used in the form of square flakes. It is a rapid-burning explosive, particularly in the flake form, and for this reason its use is confined to small-calibre weapons. It was introduced into the Service in the Great War in order to augment the supply of propellants.

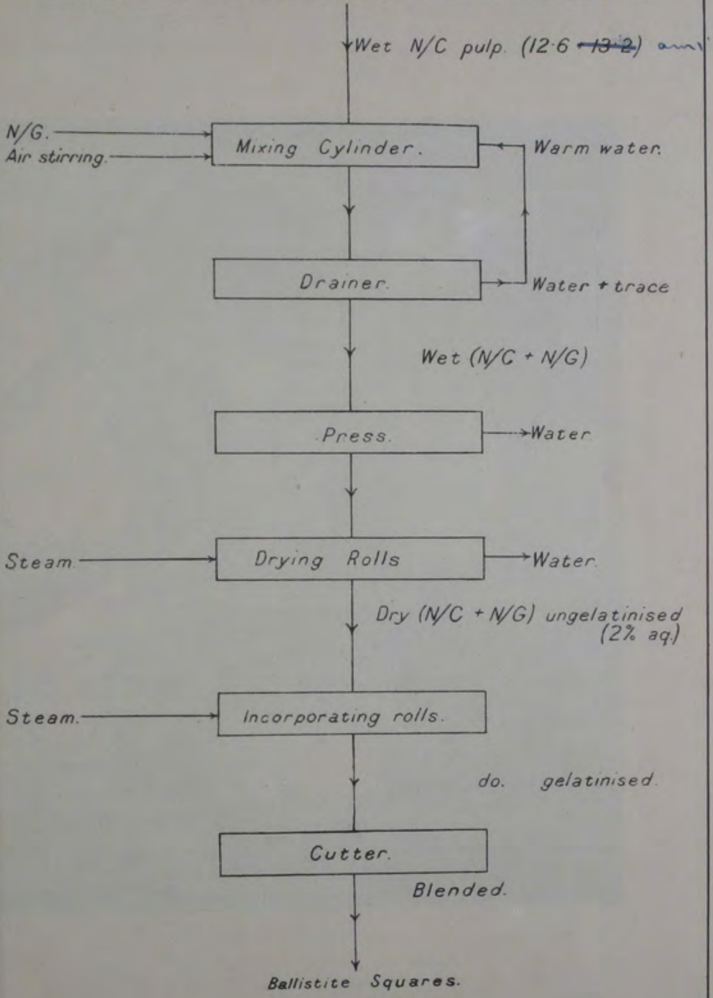
Its great disadvantage is that it is not so stable in storage as cordite. Diphenylamine and other substances such as camphor, calcium carbonate and aniline have been tried in the past as stabilizers, but the explosive is still inferior in stability to cordite.

It gives more regular ballistics than cordite, and it is rather more powerful. On the other hand, it is very much more erosive.

Ballistite is mostly used as a sporting powder, for which purpose it has been used for many years.

It has been used in other countries as a military propellant; the Italians used it in cord form under the name of "Filite", and the Germans adopted it for use in the Navy in 1898 in the form of cubes and flakes.

FLOW DIAGRAM FOR MANUFACTURE OF BALLISTITE.



N/C = "Nitrocellulose"
N/G = "Nitroglycerine"

FIG. 15.8

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Malby & Sons, Lith.

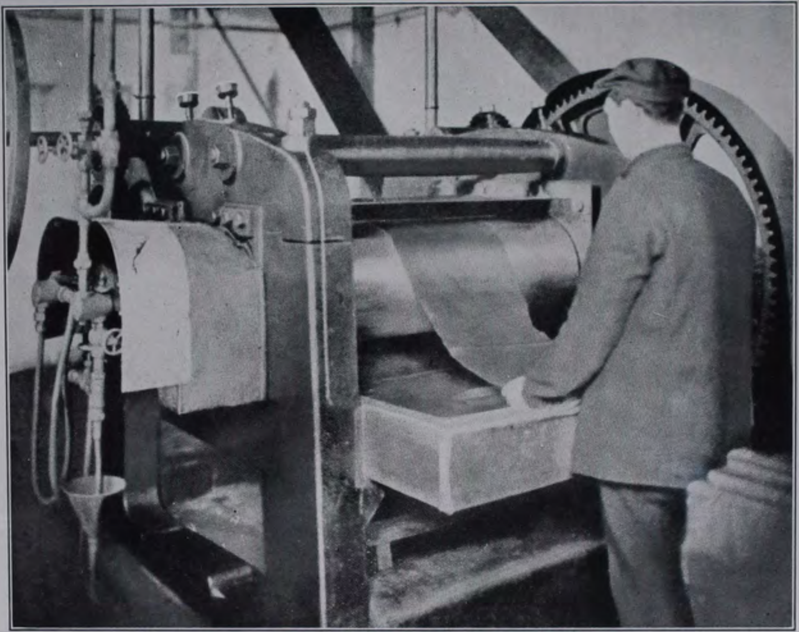


FIG. 15.9.—Ballistite Incorporating Rolls.

[To face page 110.

E.—CHEMICAL STABILITY OF EXPLOSIVES

CHAPTER XVI

STABILITY AND TESTS

STABILITY

All explosives are liable to alteration on storage to a greater or less degree. This liability depends on (i) the explosive concerned, and (ii) the conditions under which it is stored, and (iii) the presence of impurities.

The changes may be of a physical character, affecting only the general efficiency of the substance as an explosive. Two examples of this are (i) the absorption of moisture by amatol on exposure to the air, and (ii) the effect sometimes observed in the tropics, when amatol may cake together into a dense, hard mass as a result of a change in the crystalline form of the ammonium nitrate.

In some cases explosives, in which the molecule is in a state of unstable equilibrium, may suffer from chemical deterioration arising from the presence of small quantities of harmful contamination. This may render the explosive inert and therefore useless; or the decomposition may increase to the point of spontaneous inflammation.

Explosives, which are stable when pure, may be rendered unsafe by the presence of impurities, introduced in manufacture or by contamination in storage.

If the explosive is fundamentally unstable as in the case of the nitric esters, the instability is said to be *inherent;* if it is due to some external substance then the instability is called *introduced*. Introduced instability may be avoided by care and cleanliness, but inherent instability is unavoidable.

A further consideration is the general low heat conductivity of substances used as explosives. An interesting example is that of a large charge of cordite, in the middle of which is a defective, decomposing stick. In this decomposition heat is liberated. As the heat conductivity of the cordite is poor, this heat is only dissipated to a negligible extent and tends to warm up the cordite so that the rate of decomposition increases. More heat is liberated and a vicious circle is set up, so that eventually the rate of decomposition becomes such that the stick, and so the rest of the cordite, inflames.

As a class, Service high explosives are characterized by excellent stability, so much so that, with the exception of tetryl (C.E.), stability tests are not usually applied to them. If desired, the vacuum test (*see* below) may be applied; indeed, this is the only test that gives satisfactory results with high explosives, and is one of the tests applied to C.E. before it is accepted into the Service.

Another class of stable explosives is that which, like gunpowder, consists of an inorganic nitrate mixed with combustibles. Apart from the danger of their being affected by damp, they are unaffected by any ordinary conditions of storage.

Propellants all contain nitrocellulose with or without nitroglycerine, and are the most unstable explosives in general use.

Nitrocellulose and nitroglycerine are nitric esters, and as such are liable to decomposition, with the consequent formation of free acids. These acids accelerate the decomposition, and therefore great care is taken to cleanse the explosive from any waste acids that may remain after nitration. This subject has received detailed attention in Chapters XII and XIII

It has been found that, however careful the purification of nitrocellulose may be, the rate of decomposition cannot be reduced below a certain minimum (Will). The presence of impurities increases this rate, and decomposition is accelerated, particularly by oxides of nitrogen and the acids to which they give rise.

This question of the rate of decomposition is intimately connected with temperature of storage. For nitrocellulose powders, the French consider that 1 hour at 110° C. is equivalent to 1 day at 75° C. or 1 month at 40° C. (Mémorial des Poudres et Salpêtres. Vol. XV.) The Regulations for the Army Ordnance Services, Part II, give figures for cordite which indicate that a rise of temperature of 5° C. increases the rate of decomposition 1·7 times.

The decomposition of an explosive such as cordite passes through successive phases which are approximately as follows. The first sign is the formation of traces of nitrous acid (HNO_2). Gases (CO, CO_2, N_2, N_2O, NO, NO_2, etc.) are gradually evolved, and on long storage, particularly in hot climates, the cordite may undergo a visible change, losing its uniform brown colour and showing local discoloration, indicating chemical transformation and approaching danger (*see* ~~Frontispiece~~ Plate facing page 118). As decomposition advances, heat is generated, leading ultimately to spontaneous ignition. A long time, depending of course on the temperature of storage, is required before this cycle of changes is complete, but careful watch over the condition of material in the Service is necessary to ascertain that it is not approaching an unduly unstable condition.

aml

It has been found by Robertson and Napper that the oxides of nitrogen given off by guncotton while undergoing a Will Test (*see* below) at 135° C. consist approximately of 40 per cent. nitrogen peroxide (NO_2) and 60 per cent. nitric oxide (NO). The guncotton is oxidized by the nitrogen peroxide, which is thereby reduced to nitric oxide, with a reduction in the stability of the explosive.

If there is sufficient access to atmospheric oxygen, this oxidation proceeds much more rapidly, since nitric oxide is oxidized to nitrogen peroxide which then reacts on the guncotton in the above-mentioned manner. Very free access to the air will not have this effect, as the oxides of nitrogen will be dissipated before they have time to be harmful. If no oxygen whatever is present, the higher oxides of nitrogen are reduced to nitrogen and nitrous oxide (N_2O) which are innocuous. For this reason explosives containing nitrocellulose in a gelatinized form are more stable, other factors being equal, than those which are porous.

Under a Will Test at 135° C., the only nitrogenous gas evolved by nitroglycerine was found to be nitrogen peroxide. The ill effects that might be attributed to this are minimized by the fact that nitroglycerine is not so readily oxidized as nitrocellulose and therefore explosives which include nitroglycerine share this advantage to a certain extent.

The above chemical changes are considerably modified if water is present, since nitrogen peroxide (NO_2) with water forms nitric and nitrous acids which decompose nitrocellulose and nitroglycerine. Moisture is usually present to a slight extent in these explosives, and it is also a product of decomposition.

With an excess of water as, for instance, in wet guncotton, the acids are diluted, with a corresponding diminution to their effect.

Nitric acid is less injurious than sulphuric acid for two reasons: (i) it is more volatile and therefore tends to escape, and (ii) it is destroyed in its interaction with nitrocellulose. Sulphuric acid is not nearly so volatile, and its removal, by substances which will neutralize it, is therefore essential. Hence it is important that sulphuric esters should be eliminated from nitrocellulose since free sulphuric acid is formed on their decomposition.

Micro-organisms (fungi) may attack nitrocellulose and render it less stable, though this is readily avoided by the addition of a fungicide such as sodium phenate (C_6H_5ONa) to the explosive.

Particles of foreign matter, particularly metallic fragments, are harmful, as they form centres from which decomposition can spread. Care is taken to remove them in the purification processes (*e.g.* in the blanket and magnet runs described in Chapter XIII).

Stabilizers.

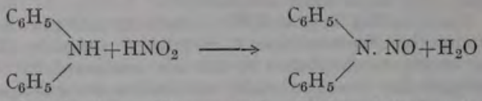
Substances, which react with the harmful products of decomposition to form innocuous compounds, are usually incorporated in explosives containing nitroglycerine or nitrocellulose.

Strong alkalies in solution cannot be employed, as their action on nitroglycerine and nitrocellulose is much more marked than is the case with acids. Therefore only alkaline substances which are practically insoluble in water (*e.g.* calcium and magnesium carbonates, $CaCO_3$ and $MgCO_3$) are employed.

Calcium carbonate ($CaCO_3$) is added to nitrocellulose; with nitric and nitrous acids it forms calcium nitrate and nitrite. Quite a small percentage is sufficient to maintain guncotton in a stable condition for many years, even under adverse conditions of storage.

In addition to these inorganic compounds, several organic substances are used. Among these are diphenylamine, mineral jelly, cracked mineral jelly, and derivatives of urea such as carbamite (*see* Chapter XIV).

The action of diphenylamine and the derivatives of urea may be exemplified by the reaction given below for the first mentioned.



Diphenylamine. Nitrous acid. Diphenylnitrosamine

Mineral jelly acts as a stabilizer by virtue of the unsaturated hydrocarbons it contains. It also prevents atmospheric oxidation by rendering the surface of the explosive impervious. If mineral jelly is subjected to the heat treatment known as "cracking," the percentage of unsaturated hydrocarbons is increased, and its stabilizing action thereby enhanced. To illustrate the formation of unsaturated compounds from a saturated hydrocarbon by "cracking," the following example of the conversion of a paraffin of high molecular weight to a paraffin of lower molecular weight plus an olefine (which is an unsaturated compound) is quoted.

$$(C_{2n}H_{4n+2} \rightarrow C_nH_{2n+2} + C_nH_{2n})$$

Paraffin. Paraffin. Olefine.

Tests

To avoid danger due to advanced deterioration, explosives which are suspect are subjected to tests, which indicate their condition. Attempts have also been made to use "auto-indicators", *i.e.* substances incorporated in the explosive, which indicate the advent of pronounced decomposition by a change of colour.

Most stability tests are based on the detection or measurement of the oxides of nitrogen liberated in a measured time at a definite temperature.

They may be divided into three main types :

(i) Trace Tests in which the first minute traces of gas given off are detected by the coloration of a delicate test paper or solution. The time for the development of a standard tint is taken as an indication of the stability of the explosive.

(ii) Fume Tests in which the explosive is heated to about 120° C. The time taken to produce distinct fumes of nitrogen peroxide, or to affect some coarse indicator such as litmus paper, is the guiding factor.

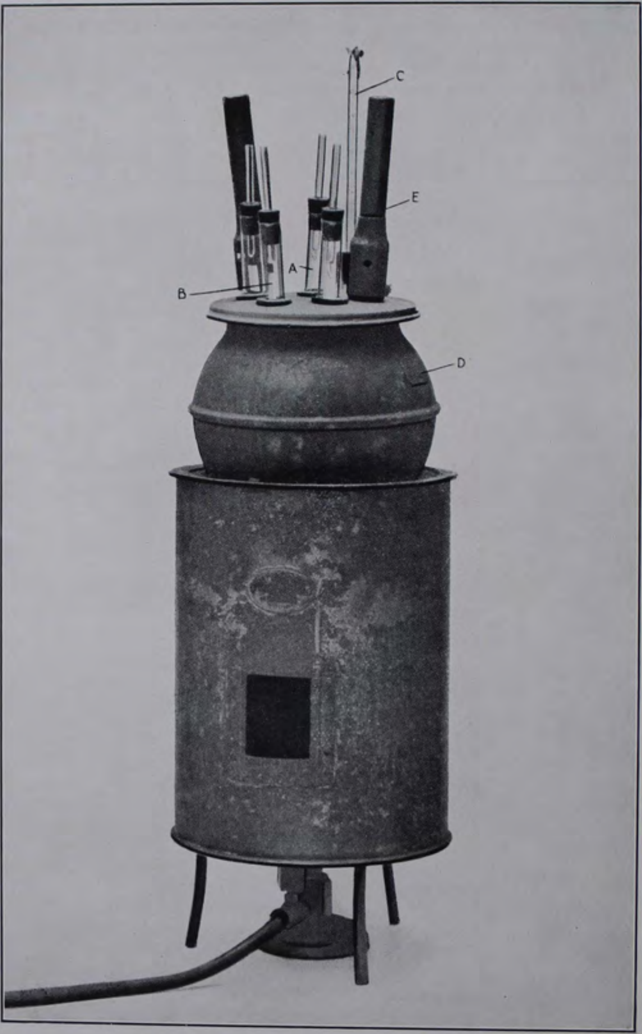


FIG. 16.1.—Apparatus for Abel's Heat Test.

(iii) Quantitative Tests in which the volume of gas evolved in a given time under standard conditions is the criterion.

Abel's Heat Test. (Fig. 16.1.)

This is the oldest stability test, and it is still the most frequently applied on account of its simplicity. For a detailed description, reference must be made to R.A.O.S., Part II.

The explosive to be tested is carefully crushed and sifted, and a sample is weighed out into a test tube (A). Suspended above the sample is a starch-potassium iodide test paper (B), which has been previously prepared under standardized conditions. The upper half of this test paper is wetted, immediately before it is used, with a non-drying solution of glycerine and water. The lower end of the test tube is immersed in a water bath (D), which is maintained at a constant temperature (usually about 80° C.) indicated by the thermometer (C). During the test the exposed positions of the tubes are protected by a cover (E) as light affects the test.

The first traces of nitrogen peroxide are detected by a change in colour at the junction of the wet and dry portions of the test paper. This assumes a brownish tint, which gradually deepens, and the test is complete when this tint matches that of a standard test paper. This test is extremely delicate, as the standard tint is produced by 0·000135 milligram of nitrogen peroxide.

The time, from the first immersion of the tube, containing the sample, in the water bath, to the development of the standard tint, is taken as a measure of the stability of the explosive. For instance, the acceptance test for new cordite M.D. lays down a minimum of 30 minutes at a temperature of 180° F. (82·2° C.). Cordite M.D. which is in the Service is required to pass a test of not less than 10 minutes at 160° F. (71·1° C.).

The Abel heat test is applicable to any explosive forming nitrogen peroxide on decomposition. It is open to certain objections arising, chiefly, from its extreme sensitiveness. The test paper can be affected by other gases than nitrogen peroxide (*e.g.* ozone), the presence of which does not necessarily imply instability. Again, the test may give false indications owing to the presence, in the explosive, of some substance, such as mercuric chloride, which prolongs the heat test by retarding the action between the test paper and the nitrogen peroxide. The test is not suitable for explosives gelatinized with ethyl acetate or alcohol, since these solvents prolong the test unduly.

The test time given by an explosive depends on a number of factors besides the intrinsic rate of decomposition of the ingredients, such as the nature of the gaseous products formed by the action of the stabilizer and their solubility in the explosive. There is therefore for each type of explosive a standard peculiar to that type. Cordite S.C., for example, though much more stable than cordite M.D. gives a lower heat test.

Other trace tests have been suggested from time to time, the main difference between them and the heat test being the use of other indicators.

Waltham Abbey Silvered Vessel Test. (Fig. 16.2 (a) and (b).)

This was a fume test originally introduced for the examination of Cordite, Mark I.

A weighed amount of cordite which has been ground and sifted, is contained in a Dewar vacuum flask, the outer jacket of which is silvered (Fig. 16.2 (b)). A thermometer ((B), Fig. 16.2 (a)), is situated so that its bulb is covered by the explosive. A side tube (A) branches off horizontally from the upper part of the neck of the vessel, to facilitate the observation of the red fumes which are given off towards the close of the test.

am 1

The cordite is maintained at a temperature of 80° C. by immersion in a bath (D), heated by a burner (E) which is controlled by a gas regulator (C). After some time, red ~~fuses~~ fumes are observed in the side tube, followed by a rise in temperature. The test is finished when the thermometer indicates a rise of 2°.

A good cordite would stand such a test for 500 or 600 hours. It was usually applied to samples of cordite which have given results under the heat test, of between four and eight minutes at 160° F.

It will be noticed that this test was intended to imitate adverse conditions of storage.

The Vacuum Test. (Fig. 16.3 (a) and (b).)

This was introduced as a stability test for tetryl (C.E.), and it is peculiarly suitable for high explosives. It is a quantitative test in that the volume of gases evolved is measured.

The apparatus consists of a test tube 15 c.c. capacity, fitted with a ground hollow stopper and a mercury cup. The stopper is joined to a capillary tube connecting with a manometer. The manometer has a reservoir at its lower end into which mercury can be introduced.

A weighed quantity (about 5 grams) of explosive is placed in the test tube and the manometer is attached, connection then being made to a vacuum pump and the apparatus is exhausted. On disconnecting the pump, the mercury runs up the capillary tube and maintains the vacuum.

The explosive is then heated to 80° C. for twenty hours, at the end of which period the apparatus is again exhausted. The explosive is now maintained at a temperature of 120° C. by the immersion of the test tube in a bath, the temperature being controlled by a thermostat or by using in the bath, a liquid which boils at 120° C. Readings are taken at intervals, comprising the following observations :

1. Temperature of bath.
2. Temperature of manometer.
3. Temperature of barometer.

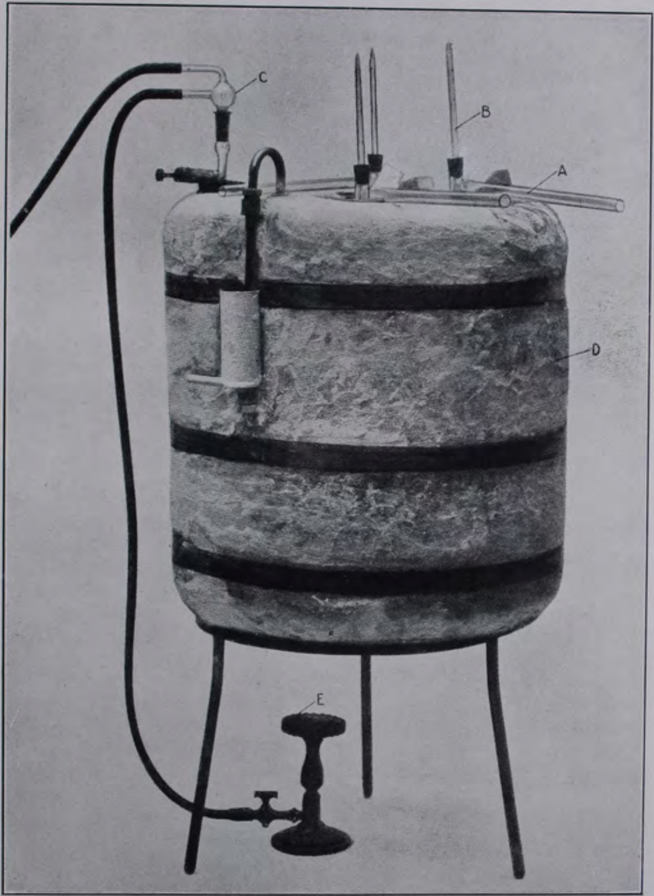


FIG. 16.2 (*a*).—Silvered Vessel Test. General Arrangement.

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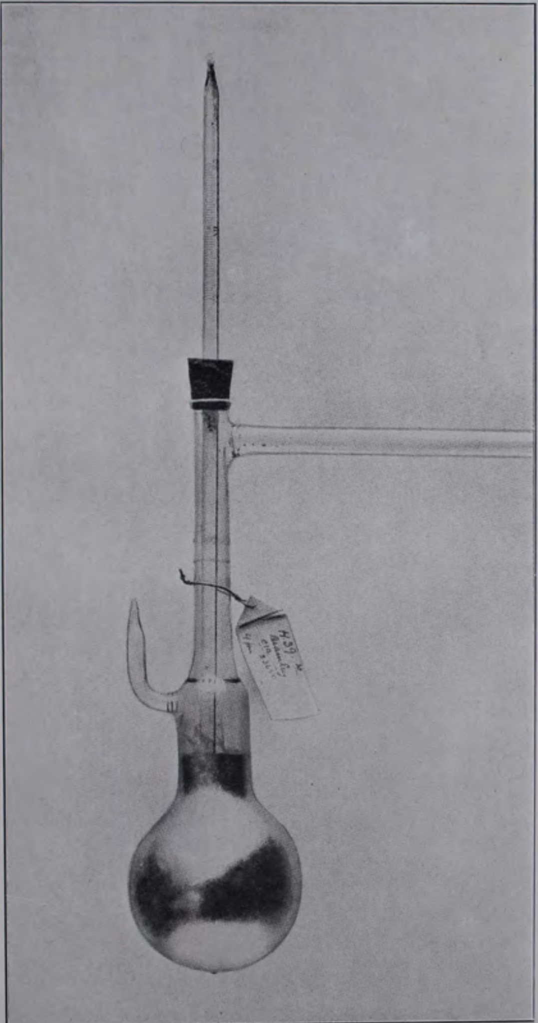


FIG. 16.2 (*b*).—Silvered Vessel.

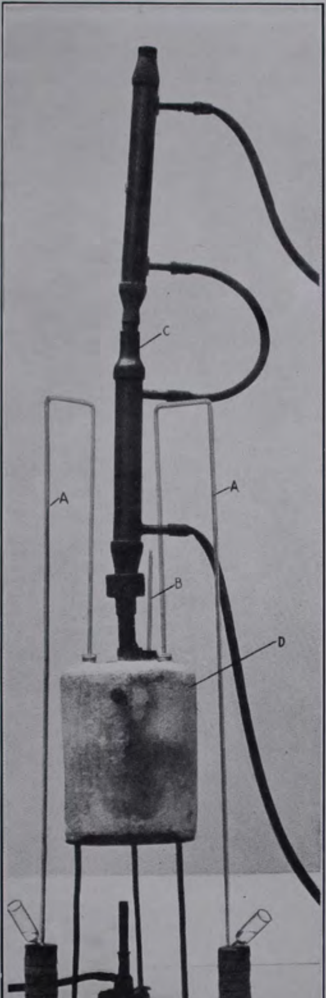


FIG. 16.3 (*a*).—Vacuum Test.

A Vacuum test in operation. The test tubes (seen at A Fig. 16.3 (*b*)) are immersed in the bath (D), the necks just being visible above the top of the bath. The manometers leading from them (A, A) are plainly visible. C is a condenser which condenses and returns as liquid the vapour of the substance used in the bath, the temperature of which is shown by the thermometer (B).

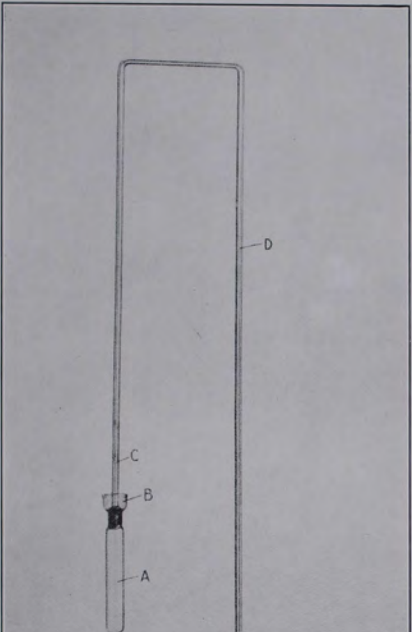


FIG. 16.3 (*b*).—Detail of Vacuum Tube and Manometer.

The tube containing the explosive is shown at (A). Above the neck of the tube can be seen the small trough (B) surrounding the capillary tube (C). Mercury can be introduced into this trough where it serves as a seal. The capillary tube (C) leads to the manometer (D) at the lower end of which is the reservoir for Mercury (E).

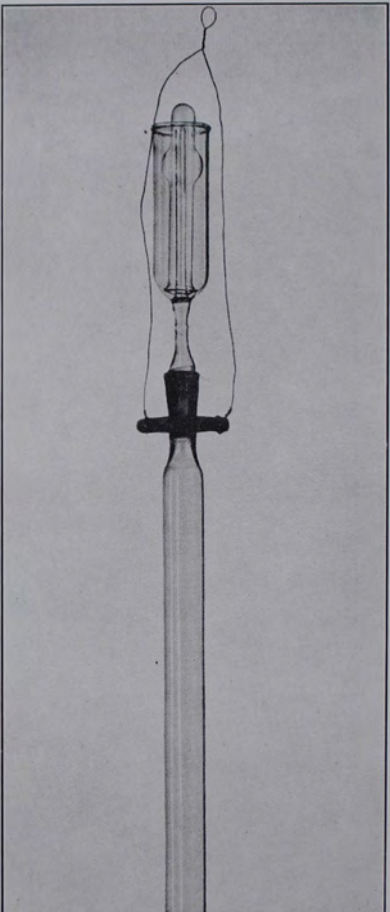


FIG. 16.5 (*b*).—Test Tube and Absorption Bulbs for Bergmann and Junk Test.

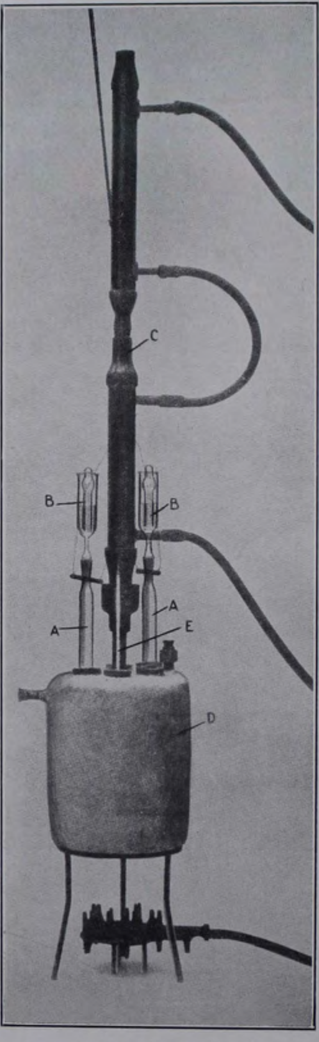


FIG. 16.5 (*a*).—Bergmann and Junk Test. General Arrangement.

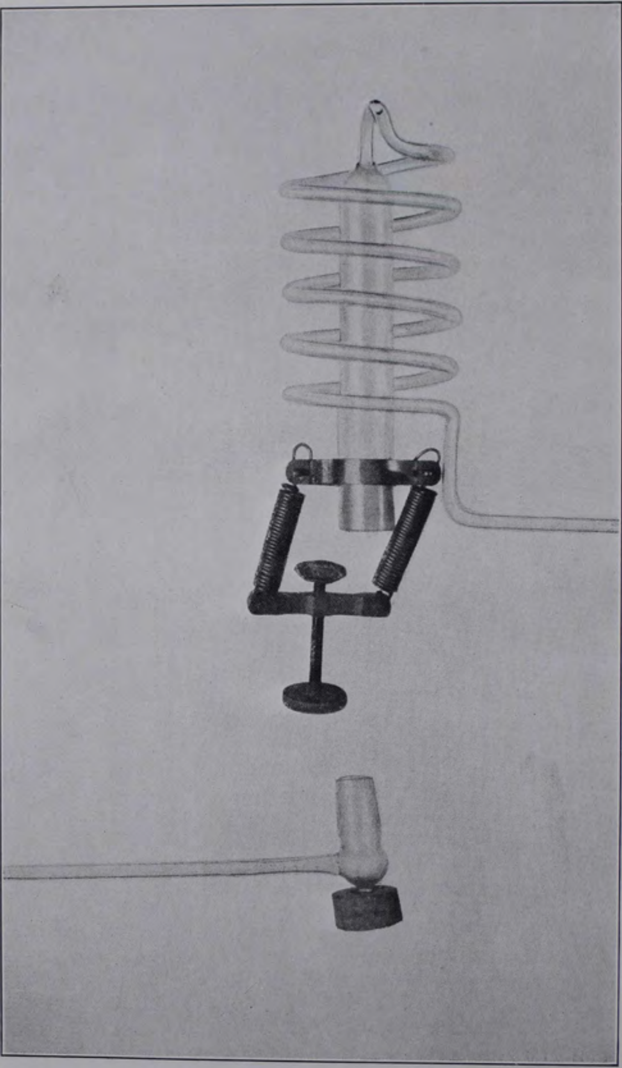


FIG. 16.4 (*c*).—Detail of Combustion Tube. Will Test.

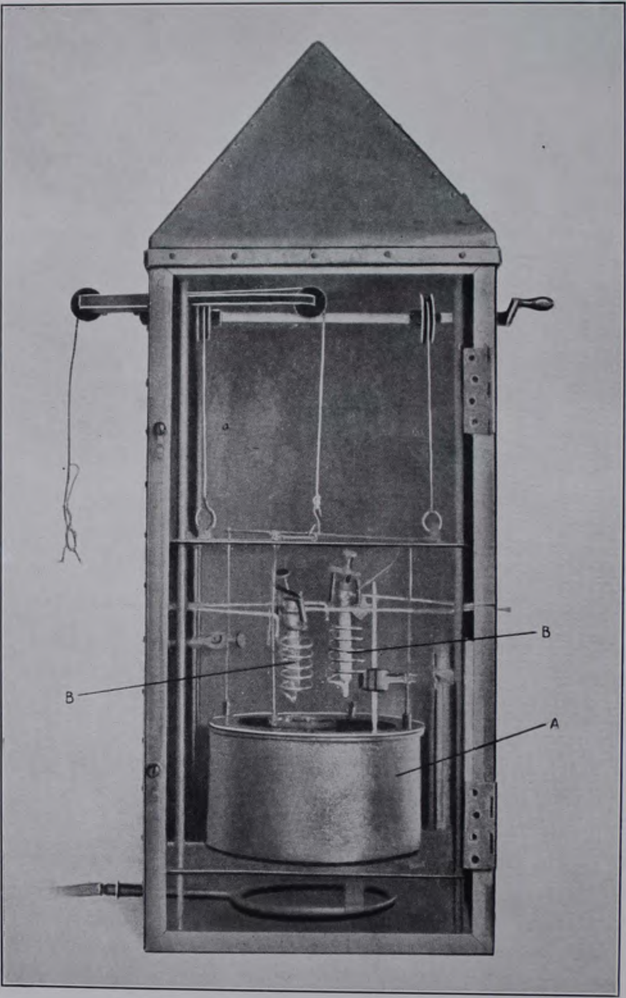


FIG. 16.4 (*b*).—Detail of Apparatus for Will Test.

This is a close view of the test tube and bath. It shows the thermometer which indicates the temperature of the bath (A), the means of raising and lowering the bath (which is shown in the lower position) and two combustion tubes (B, B).

To face page 117.]

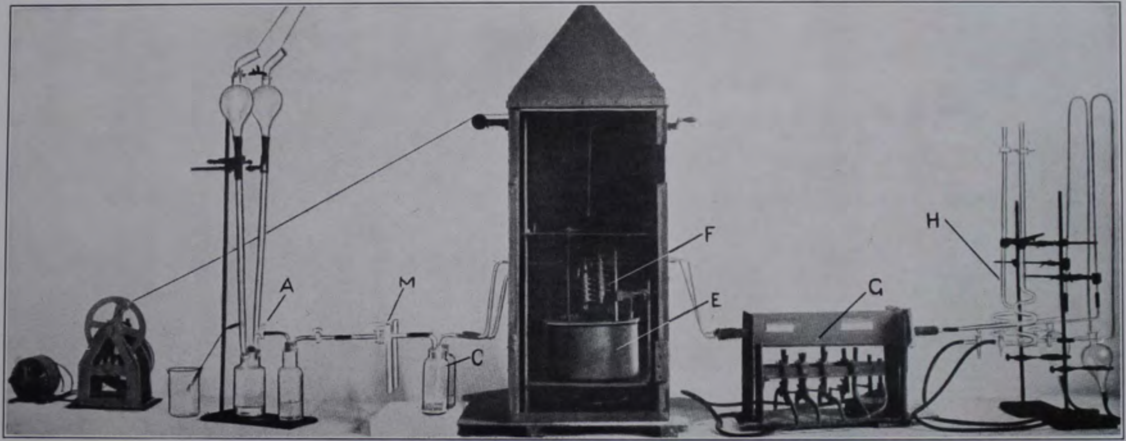


FIG. 16.4 (*a*).—General Arrangement of Will Test.

On the left side at (A) is the apparatus for generating Carbon Dioxide by the interaction of Sulphuric Acid and Potassium Bicarbonate contained in solution in the two vessels. The rate of flow and purity of the gas are ensured by the manometers (M) and the wash bottles (C). The Carbon Dioxide is then led into the test tube (F) by the spiral shown. When the test is in operation the bath (E) is raised so as to surround the test tube, by means of the rope and pulleys shown. The combustion tube is shown at (G) from whence the mixture of Carbon Dioxide and Nitrogen is led to the special burettes (H) containing a solution of Potassium Hydroxide.

4. Height of mercury in manometer.

5. Height of mercury in barometer.

The first reading is taken 1½ hours after the introduction of the apparatus into the bath, followed by three readings per day for two days, or until the total evolution of gas is 4 c.c.

For the calculations, the volume of the test tube, the volume of explosive, and the volume of unit length of the capillary must be known. The volumes of gas recorded require correction to normal temperature and pressure (0° C. and 760 mm. of mercury).

Not more than 4 c.c. (corrected) of gas should be evolved in 40 hours at 120° C. by tetryl under the conditions of this test.

Will Test. (Fig. 16.4 (a), (b) and (c).)

This test, which is usually applied to nitrocellulose, is a quantitative test.

The explosive is heated to a temperature of 135° C. in an atmosphere of carbon dioxide. The nitrogenous gases evolved are reduced to elementary nitrogen in a combustion tube containing metallic copper and copper oxide at a red heat ; this also serves to convert the organic gases which are evolved to carbon dioxide and water. The volume of nitrogen so obtained is measured in a gas burette filled with potassium hydroxide solution in which carbon dioxide is readily absorbed.

2·5 grams of good service guncotton should not ~~will~~ yield more than 4·5 to 6·5 milligrams of nitrogen in four hours. Amm 1

Bergmann and Junk's Test.—132° C. Test. (Fig. 16.5.)

This quantitative test is an alternative to the Will test, and is now more frequently applied as it is quicker and the apparatus is much more simple.

The nitrocellulose to be tested is pressed between filter papers and dried for 6 hours at 50° C. After cooling, it is passed through an IMM Standard 50-mesh sieve. The sample before test should contain a minimum quantity of moisture. Two grams of the sieved sample are placed in two of three glass tubes, one of which is used as a blank.

The two test tubes (A, A), after being fitted with absorption bulbs (B, B) containing 30 to 40 c.c. of distilled water, are mounted in copper tubes in the heating bath (D). They are then maintained at a constant temperature of 132° C. for two hours. In Fig. 16.5 (a) (C) is a condenser for condensing and returning the vapour from the liquid used in the bath. A liquid having a boiling-point of 132° C. is used.

On cooling, some of the water in the absorption bulbs is drawn into the test tubes, the remainder being poured into a flask. To the water in each test tube, and to the contents of the blank, 20 c.c. of N/10 hydrochloric acid are added. After corking, the contents of the tubes are shaken for 15 minutes and then filtered. Care is taken to remove all acid by careful washing.

To the solutions from the heated samples and from the blank 25 c.c. of N/10 potassium hydroxide solution are added The excess of alkali present is then estimated by titrating with N/10 hydrochloric acid, using methyl orange as an indicator

Then if A=number of c.c. of N/10 Hydrochloric acid titrated in the case of the heated sample, and B is the corresponding figure for the blank experiment, then the amount of nitrogen liberated per gramme of nitrocellulose is

$$0{\cdot}7\ (B-A)\ \text{milligram}$$

Climatic Trials

The deterioration of explosives at tropical temperatures of storage is sometimes ascertained by " climatic " trials, in which the explosive is stored in chambers, artificially heated to regulated temperatures, in either a dry or a moist atmosphere. Moisture has an important influence on the rate of deterioration

One of the most important cases of failure under high temperature of storage is that of fuse detonators containing mercuric fulminate. Trials have shown that the 4 and 5 grain detonators may become useless after a period of three months at 140° F.

The larger detonators which contain a mixture of mercuric fulminate and potassium chlorate do not appear to be quite so susceptible to high storage temperatures, but they are adversely affected in time.

Lead azide does not suffer from this disadvantage, and herein lies one of the main arguments in favour of its adoption for tropical service.

The Colour Test of S.C. and W. cordite. (For carbamite cordites.)

The colour test is a measure of the amount of stabilizer which has been used up during the life of the cordite in combining with the acid products of decomposition. The bodies so formed produce a coloured solution when the cordite is dissolved in acetone and the intensity of the colour of this solution is compared with those of various standard colour solutions of graded intensity. The darker the colour of the solution, the less is the amount of carbamite left ; and the condemning limit is reached when the cordite contains only half of its original carbamite content.

In practice, the colour test (which is described fully in R.A.O.S., Pt. II) is carried out by matching, in a colorimeter, the colour of a solution of one gram of cordite in 50 m.l. of acetone against a standard solution which represents the colour produced by a sample of cordite which retains only half of its original carbamite content. The standard solution used in the testing of S.C. cordite has the composition :

Potassium bichromate ($K_2Cr_2O_7$) ...	... 1·2 grams	Made up to one litre with water
Cobalt ammonium sulphate $Co(NH_4SO_4)_2 6H_2O$ ...	... 32·7 ,,	
Concentrated sulphuric acid ...	... 12·5 m.l.	

PICTORIAL REPRESENTATIONS OF CORDITE.

SHEET 1.

1

2

3

4

5

1.
2. NEWLY MADE CORDITE.
3. SHOWING RANGE IN COLOUR.
4.

5. EARLY STAGE OF CORROSION OF CORDITE MD. SIZE 16.

Wt. 28031/8534. 10/38. F. & C. Ltd.

PICTORIAL REPRESENTATIONS OF CORDITE.

SHEET 2.

6

7

8

9

6. INTERMEDIATE STAGE OF CORROSION OF CORDITE MD. SIZE 19.
7. ADVANCED STAGE OF CORROSION OF CORDITE MD. SIZE 16.
8. ADVANCED STAGE OF CORROSION OF CORDITE MD. SIZE 8.
9. CORDITE CONTAINING AIR BUBBLES.

The Colour Number of the cordite is recorded as

$$25 \times \frac{\text{Depth of column of standard solution}}{\text{Depth of column of cordite solution}}$$

When the colour number reaches 25, the cordite is condemned. If the colour number is 5 or smaller, the colour is found by direct comparison of the cordite solution against standard solutions having colour numbers of 1 to 5.

The hundred per cent. surveillance test.

The 100 per cent. surveillance test is applied to mineral jelly cordite in bulk, and in B.L. charges, and is designed to indicate whether the cordite in any package is approaching a dangerous condition. Each package is provided with a glass window through which can be seen a coloured test paper which is exposed to the air inside the package. The test paper is stained with a chemical "indicator," which is affected by the gases given off by the cordite during storage, and gradually changes colour. With new cordite, the change in colour takes place in the course of several months, the duration of the test depending on the temperature of storage. As the cordite ages, the test tends to become shorter. When the cordite is reaching a dangerous condition, it takes place in a few days. Individual packages containing cordite which for any reason has deteriorated more rapidly than that in similar packages containing the same lot, will be indicated by the papers changing in colour markedly more rapidly.

It is essential to ensure, for the gases, as free a path as practicable, between the cordite and the test paper.

The original colour of the test papers is blue and on exposure to the gases emanating from the cordite, it changes gradually to a purplish-red. The range of colours is illustrated on a chart (Fig. 16.6, *Frontispiece*). If test papers are left in contact with the gases from cordite beyond this point, the red colour becomes brighter and resembles that shown at the right side of the chart. The purplish-red colour designated as "F" on the chart is taken as the end-point of any test.

Two types of test paper are issued, namely C.B.H. for hot, and C.B.T. for temperate magazines. For the purpose of this test, temperate magazines are defined as those in which the mean annual temperature is 70° F. and below ; hot magazines are those in which the temperature is above 70° F. The C.B.H. papers are punched with a small hole to facilitate recognition.

The test papers are of a sensitive character and it is important that when they are not in use, the pads should always be stored sealed up in the canisters in which they are supplied, in a cool, dry place away from acid fumes. The test papers are affected by material containing iron (scissors, knives, etc.), and should not be trimmed nor cut except with bronze scissors.

The change of colour of test papers is sometimes uneven during protracted tests on account of the masking effect of the window fitting, but when rapid tests occur the effect is of little significance. It does not, for example, appear to have caused any difficulty at Malta, where a large number of short tests have been observed. In such cases of uneven tinting, the observer takes the most advanced tint on the paper as his datum in sentencing the cordite under test.

In order to facilitate the work of the observers, standard end tints are provided. They can be carried round the magazine and used for comparison with the tints in the cordite packages under identical conditions of lighting. To prevent the tints from fading, the boxes containing them should be kept shut when not in use and stored with the same care and precautions as are observed with the test papers. Fresh standard end tints in boxes will be issued every two years to prevent the use of any which may have become faded or damaged.

Packages for test should be stacked in the magazine in such a manner that the " inspection " windows are easily accessible for inspection and renewal of test papers.

Inspection. The test papers are examined at intervals to ascertain whether they have reached the end tint. The intervals between inspections are indicated in the following table :

TABLE 16.A.

100 PER CENT. SURVEILLANCE TEST OF CORDITES. FREQUENCY OF INSPECTION (B.L. AND BULK).

Average temperature of magazine	Inspection period
80°–90° F.	Every 2 days
70°–80° F.	Twice weekly
70° and below	Weekly

On reaching the end tint, the test papers should be changed, the new paper bearing the date of change. In any case they should not remain in the cordite packages longer than six months.

Sentencing.

(i) Packages in which the test papers reach the end tint in less than eight weeks are to be regarded as under suspicion ; they should be placed in an easily accessible position in the magazine and specially watched.

(ii) When the test time falls to four weeks or less, the procedure is as follows :

(*a*) Where the test has been installed for less than 12 months, the packages are removed from the magazine and segregated. The contents are broken down, inspected visually and tested by such tests as are applicable to the type of cordite concerned.

(*b*) Where the test has been installed for more than 12 months.

The cordite is examined and sentenced unserviceable, and samples of the worst material from the deteriorated charge are selected. The remainder of the cordite is destroyed.

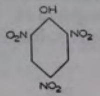
F.—MANUFACTURE OF HIGH EXPLOSIVES AND THE SUBSTANCES ENTERING INTO THEIR COMPOSITION

CHAPTER XVII

PICRIC ACID, DINITROPHENOL, SHELLITE, PICRIC POWDERS

The substances for consideration in the next four chapters are those used either as shell fillings or as part of the chain of intermediaries between the initiating detonator and the final explosive to be detonated.

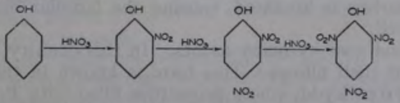
Picric Acid, or S.—Trinitrophenol.



Introduction.

A brief account of the history of picric acid has been given in Chapter III. The remarkable fact in its history is the long period that elapsed between its discovery by Woulffe in 1771, and its first recognition as a powerful high explosive about 1880. This points at once to the highly insensitive nature of picric acid.

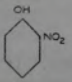
Picric acid is a true nitro-compound, trinitrophenol. The stages in the nitration of phenol may be shown for the purposes of illustration thus :



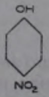
Phenol. 0. Mononitro-phenol. 2, 4. Dinitro-phenol. Symmetrical Trinitrophenol.

Trinitrophenol cannot be made satisfactorily by the direct action of nitric acid on phenol.

(i) With dilute nitric acid, the resultant product is a mixture of two mononitrophenols ;



Ortho-nitrophenol.

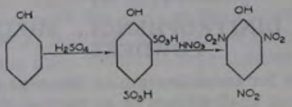


Para-nitrophenol.

(ii) With concentrated nitric acid, much loss is caused by oxidation.

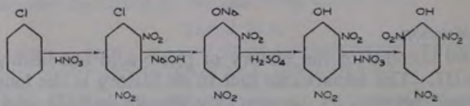
Trinitrophenol is readily obtained by a number of indirect methods.

(i) The oldest process is nitration through phenol-sulphonic acid, which can be made by the direct action of sulphuric acid on phenol.



Phenol. 1. Phenol 2, 4. disulphonic acid. Picric acid.

(ii) From chlorbenzene, obtained by the direct chlorination of benzene. This process is important, as it furnishes a means of obtaining dinitrophenol which is itself important as a constituent of high explosives.

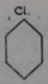


Chlorbenzene. 2, 4. Dinitrochlorbenzene. Sodium *m*-dinitrophenate. 2, 4. Dinitrophenol. Picric acid.

Picric acid is deficient in oxygen, with the result that on detonation, free carbon is liberated, causing the familiar black burst of a lyddite shell.

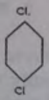
Picric acid goes by many names. In this country, it is melted and cast for shell fillings. This form is known in the Service as lyddite. (From Lydd, where projectiles filled with P/A were first tried out.) In France (with collodion), it is known as melinite ; in Japan, as shimose powder ; and in Germany as Granatfüllung C/88.

Chlorbenzene C_6H_5Cl.



This compound is a derivative of benzene. It is readily made by passing chlorine into benzene until chlorination to monochlorbenzene has taken place.

p-Dichlor benzene is also formed at the same time, but is easily separated from monochlorbenzene by fractional distillation; the former boils at 179° C. and the latter at 132° C.



Para Dichlor Benzene

The Manufacture of Picric Acid

I. FROM PHENOL.

(*a*) *Old Pot Process.*

This is the old process that was in vogue prior to 1914. It has been improved to such an extent that a modern plant bears very little resemblance to the original. These improvements have not altered the underlying principles so much as they have provided for greater economy in working, by the recovery of waste acids and fumes.

The process may be divided into three main headings:

1. Sulphonation.
2. Nitration.
3. Purification.

1. Sulphonation.

Phenol and sulphuric acid, in the proportions by weight of 1 to 4·5, are run into rectangular, steam-heated tanks. The temperature is maintained at 80° C. for 12 hours, by which time the phenol has been converted into the disulphonic acid, with a little of the monosulphonic acid.

The sulphonic acids are allowed to cool, and are diluted with waste liquor from a previous operation to about half their original strength. The contents of the tanks are then allowed to stand, so as to permit any solid matter present to settle.

2. Nitration.

The phenol disulphonic acid is weighed out into charges corresponding to about 35 lb. of phenol; each charge being contained in a 40-gallon earthenware pot.

Nitric acid (65 per cent. strength) is syphoned slowly into the pots. The temperature rises, and copious red fumes of nitrogen peroxide are given off. Means are provided by which these fumes are collected and conveyed to the absorbtion towers for recovery.

The contents of the pots are kept at 110° C. for 48 hours, and are then allowed to cool. The picric acid crystallizes out on cooling.

3. Purification.

This will be described later.

The essential stages of this process are given in the form of a flow diagram in Fig. 17.1; a nitrating house being shown in Fig. 17.2.

(*b*) *Brooke's continuous process.*

This process, while chemically the same as that just considered, is entirely different in detail, being much more economical by virtue of the more thorough recovery of waste products and the greater saving in labour. It was worked out at Brooke's Chemical Works, Halifax, during the latter half of the Great War.

The sulphonation is carried out as already described, and, after dilution, the phenol sulphonic acid is conveyed to the nitrating plant, Fig. 17.3.

This consists of an acid-proof brick trough, about 160 feet long. Along this trough the phenol sulphonic acid slowly flows, and at frequent intervals nitric acid is introduced through a system of aluminium jets. Complete nitration is ensured by (*a*) regulation of the rates of flow of the liquids; and (*b*) maintenance of the temperature at about 100° C. by means of steam coils in contact with the trough.

At the lower end of the trough, the picric acid and spent nitrating acids flow over a weir, where the picric acid crystallizes out.

The separation and purification of the picric acid is carried out in the manner to be described later.

(*c*) *Strong acid nitration* (*Bradley*).

This process is essentially the same as the old pot process as far as the sulphonation of the phenol is concerned.

The nitration is accomplished, using a mixture of strong nitric and sulphuric acids, in enamelled nitrators fitted with stirrers.

(*d*) *Nitration using sodium nitrate.*

A process on these lines has been worked in France. Sodium nitrate is used instead of nitric acid. Great economy is claimed for it, but the Armistice in 1918 prevented its full development.

II. FROM CHLORBENZENE.

The chemical reactions involved have been considered in the earlier part of this chapter.

The process is divisible into five stages:

(i) Nitration to dinitrochlorbenzene.
(ii) Conversion to sodium dinitrophenolate.
(iii) Liberation of dinitrophenol.
(iv) Nitration to picric acid.
(v) Purification of the crude picric acid.

(i) Nitration to dinitrochlorbenzene.

Chlorbenzene is nitrated with a mixture of nitric and sulphuric

FLOW DIAGRAM FOR MANUFACTURE OF PICRIC ACID.

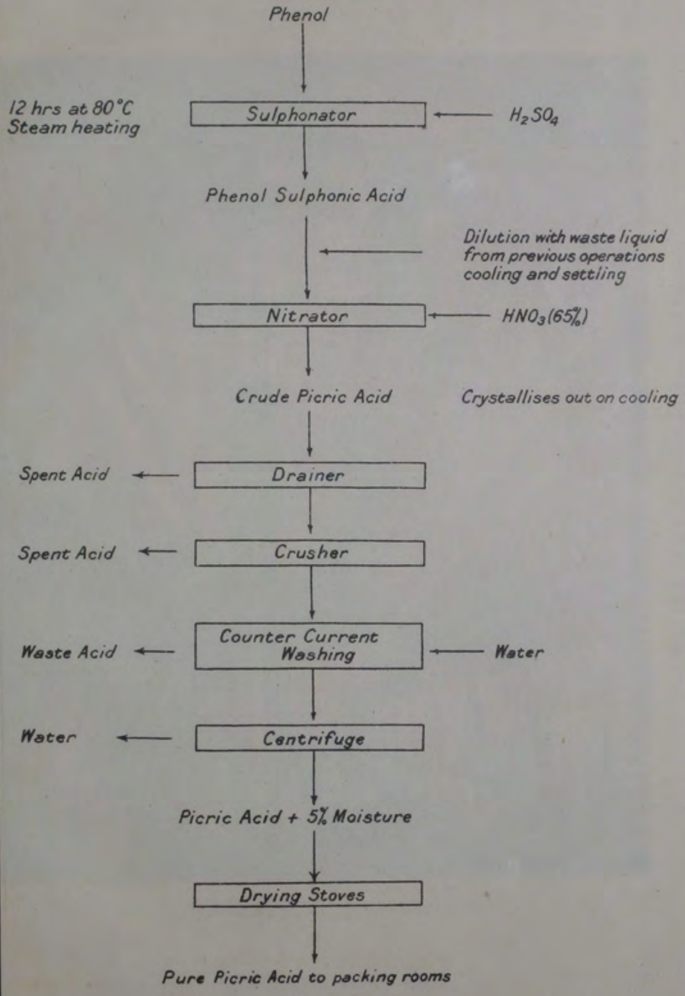


FIG. 17.1.

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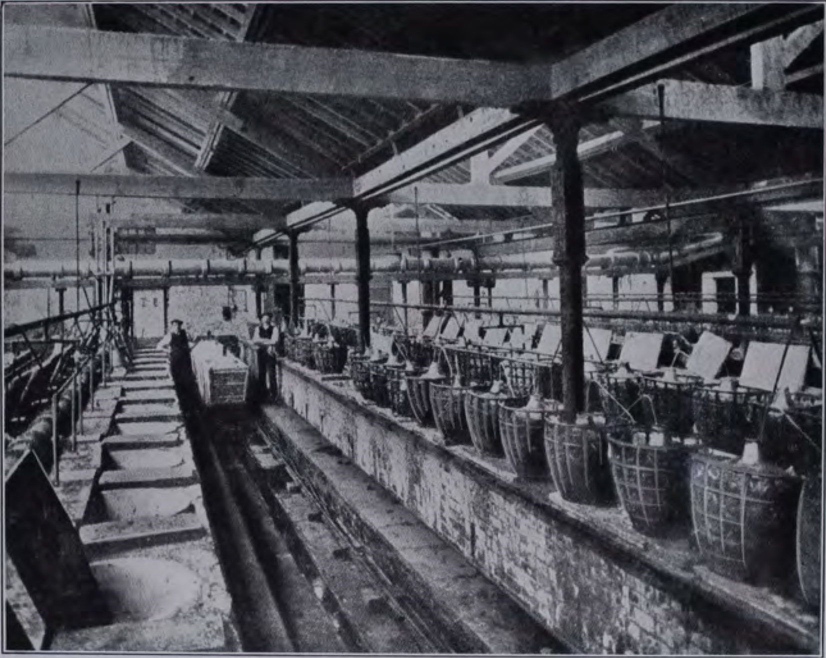


FIG. 17.2.—Picric Acid Manufacture. Pot Process.

[*To face page* 124.

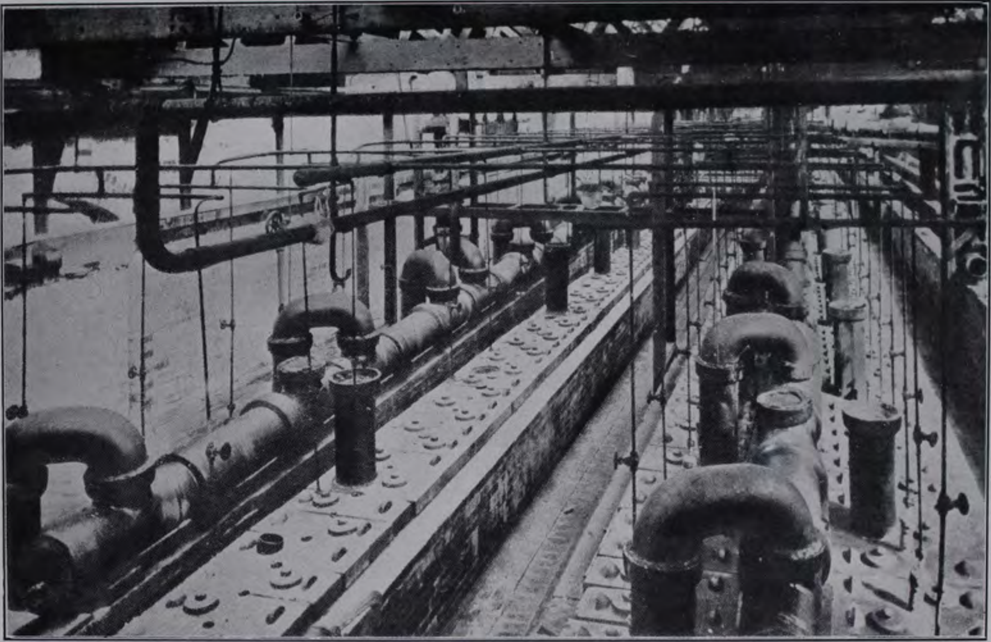


FIG. 17.3.—Picric Acid Manufacture. Continuous Process.

acids, and the dinitrochlorbenzene separates out as a solid which melts at 53° C. The action proceeds quite quietly. Dinitrochlorbenzene must be handled very carefully as it is irritating to the skin and poisonous.

(ii) Conversion to sodium dinitrophenolate.

The product from the previous operation is heated by steam in a boiler containing a solution of caustic soda (NaOH). The sodium salt is formed and remains in solution.

(iii) Liberation of dinitrophenol.

On acidification of the solution from (ii) with sulphuric acid, sodium sulphate is formed and remains in solution, the insoluble dinitrophenol being precipitated.

(iv) Nitration to picric acid.

The dinitrophenol is recovered by filtration and is treated with a mixture of strong nitric and sulphuric acids. Enamelled nitrators, fitted with stirrers, are used ; the temperature is kept a little above 100° C.

(v) Separation and purification of the crude picric acid.

This is carried out in the usual manner.

Separation and purification of crude picric acid.

Picric acid does not lend itself to purification by recrystallization, and therefore a system of washing and drying is employed. The method adopted may be considered under six headings :

(i) *Draining.*

To remove spent acid from the crude picric crystals.

(ii) *Crushing.*

To free spent acid that has been trapped among the picric acid crystals.

(iii) *Counter-current washing.*

This is a very general method of purification in industrial chemistry, and is described in Appendix III.

(iv) *Centrifuging.*

This reduces the moisture content to about 5 per cent.

(v) *Stove drying.*

The last traces of moisture are removed by this means. The picric acid is spread on glass trays in drying chambers, the temperature of which is maintained at 60° C. This is the most dangerous stage in the manufacture of picric acid and it is therefore carried out in buildings situated at a safe distance from the remainder of the works.

(vi) *Sifting.*

Reel sifters are employed.

Properties and Uses

Picric acid is a yellow crystalline solid, melting at 121·6° C. It has a very bitter taste, whence its name from the Greek " pikros," meaning bitter. Owing to its intense yellow colour it was employed for many years as a dye.

When unconfined, it burns quietly, with a very smoky flame.

It is an acid, forming salts, called picrates, with most metals. Some of these salts are extremely sensitive, and the readiness with which they are formed constitutes the main disadvantage attending the use of picric acid.

Below is a table of the figures of insensitiveness of the commonest picrates (picric acid=100). (*See* Chapter V.) The figures given apply to the picrate in the state of hydration in which it would be formed at normal temperatures. When rendered anhydrous, certain of the picrates become more sensitive.

TABLE 17.A

Picrate	*Figure of Insensitiveness*
Lead	18
Barium	68
Sodium	80
Copper	90
Zinc	110
Nickel	110
Ammonium	110
Calcium	over 120

Lead picrate is particularly sensitive, and the ignition of a small quantity will initiate detonation of picric acid in contact with it, Great care must therefore be taken to ensure that the quantity of lead compounds present in paints, metals and materials with which picric acid is likely to come in contact, either in its manufacture or use, is restricted to a very small percentage.

To avoid any possibility of lyddite in shell becoming sensitive owing to the formation of iron picrate, the interior of the shell bodies is coated with copal varnish.

Ammonium picrate, on the other hand, is comparatively insensitive, and forms an important constituent of some mixed high explosives used as intermediaries. It is used in U.S.A. as a filling for armour-piercing shell.

Picric acid is soluble in water to the extent of 1 part in 100 parts of cold water, and 1 part in 20 of hot water. It is readily soluble in benzene, and many organic solvents.

Owing to the high melting-point of picric acid it cannot be melted over a water bath, and other means of heating are therefore used.

Picric acid is very stable, and maintains its stability so well under the most adverse conditions, that stability tests are not usually applied. As high temperatures of storage over long periods cause no deterioration, lyddite-filled shell are particularly suitable for tropical stations.

The tests for picric acid can be obtained from the specification, to which the reader is referred. The underlying reasons for these tests are given where necessary in the following:

(i) The melting-point test.

This detects the presence of dinitrophenol, which lowers the melting-point. M.P. must be *not* below 120° C. and *not* above 121·6° C.

(ii) Volatile matter.

The percentage of volatile matter is an indication of the amount of moisture and unnitrated bodies present.

(iii) Ash content.

Besides detecting the presence of grit and other extraneous solid matter, this test is important as a means of locating any sensitive picrates formed in process of manufacture of the picric acid.

(iv) Test for the presence of sulphates.

As the sulphates that are most likely to occur are soluble, this test is a check on the efficiency of the purification.

(v) Oxalates or picrates absent. Picrates are apt to be very sensitive, *see* Table 17.A.

(vi) Matter insoluble in water *not* to exceed ash content by 0·05 per cent.

(vii) When 50 grams of the material are melted in a test tube a yellow to light brown liquid is obtained. This liquid, when maintained at 143° C. for one hour, must *not* appreciably darken and *not* more than a trace of scum or deposit must be present.

(viii) Matter insoluble in benzene when dried in a boiling water oven for 2 hours, must not exceed sulphated ash content by more than 0·1 per cent.

Dinitrophenol and Shellite

Preparation.

Dinitrophenol can be conveniently prepared by the chlorbenzene process, outlined above, omitting the final step.

Properties and uses.

Dinitrophenol is a yellow-brown crystalline compound melting at 110°–114° C., according to its state of purity, the purer product having the higher melting-point.

In an unconfined state it burns quietly with a very smoky flame. It is poisonous, and should therefore be handled with care. It is somewhat less sensitive than picric acid.

It is chiefly important in this country as a constituent of shellite.

Shellite

This is a high explosive consisting of a mixture of dinitrophenol and picric acid.

It melts at about 76° C., and hence it may be melted on a water bath.

Its stability is much the same as that of picric acid, and it is rather more insensitive (figure of insensitiveness 124. Picric acid =100).

Picric Powder

Composition.

Ammonium picrate	43 parts
Potassium nitrate	57 parts

Properties and uses.

On ignition this mixture rapidly develops explosive violence, and is capable of initiating a violent explosion, usually somewhat less than complete detonation, in most high explosives. It is therefore valuable as an intermediary in ammunition in which for any reason an initiatory detonator is not used.

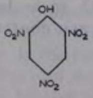
Another mixed explosive using ammonium picrate is *picramite :*

Ammonium nitrate	72
Ammonium picrate	28

(*See* Chapter XX.)

Toxic degradation product of picric acid—Chloropicrin

If picric acid be treated with bleaching powder, the benzene ring breaks down and one of the products is chloropicrin (nitrochloroform) $Cl_3.C.NO_2$, this being derived from the three ($C-NO_2$) groups in the picric acid molecule. Chloropicrin is a powerful lung injurant and lachrymator. It was used thus in the Great War.



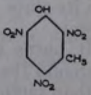
$+ 9\ Cl \longrightarrow 3\ Cl_3.C.NO_2$ + Other products.

(from bleaching powder.) Chloropicrin.

Picric Acid

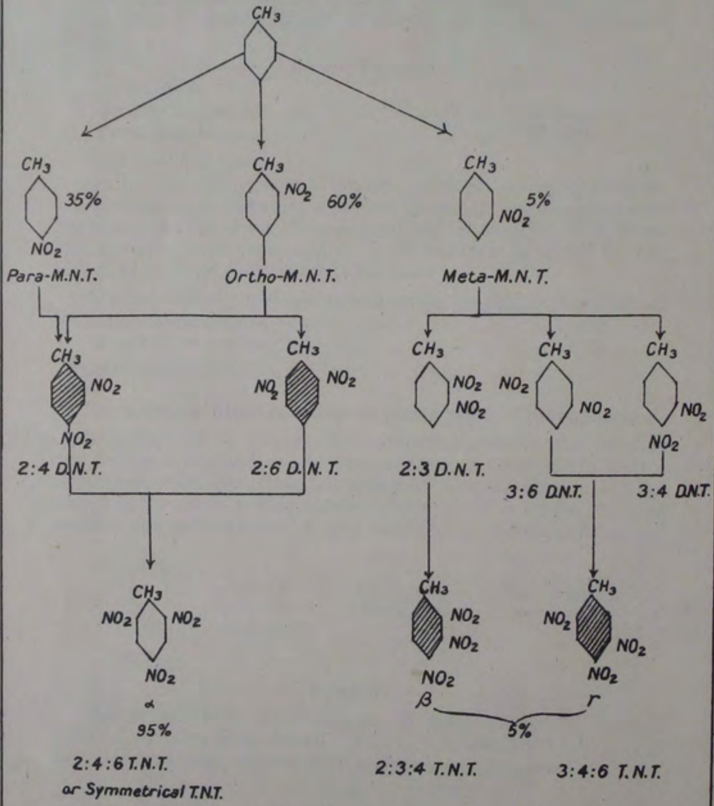
Cresylite

The French have used cresylite or 2.4.6. trinitro 3 methyl-1 phenol (trinitro meta cresol). This is very similar to picric acid and, although more expensive to make, conserves phenol.



Cresylite.

NITRATION OF TOLUENE.



The Isomers which cause exudation are shaded.

FIG. 18·1.

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CHAPTER XVIII

TRINITROTOLUENE, AMATOL, BARATOL

(Throughout this chapter, the initials M.N.T. and D.N.T. are used to denote mononitrotoluene and dinitrotoluene respectively.)

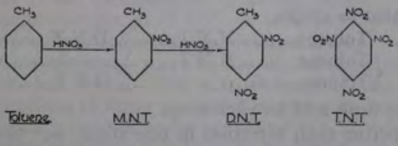
Trotyl, Trinitrotoluene, or T.N.T.

Introduction.

This compound was discovered in 1863 by Wilbrand, but prior to 1914 was not used in the Service as a shell filling, though it had been employed by the Germans since 1902. Its development as a Service high explosive in this country was undoubtedly handicapped by the difficulty that was experienced in designing an adequate exploder system.

At the commencement of the Great War T.N.T. became important as a possible source from which to supplement the supplies of high explosive. Some idea of the immense progress made in the manufacture of T.N.T. during the war may be gained from a comparison of the output during the first six months of the war (143 tons), with the total output at the time of the Armistice in November, 1918 (238,364 tons).

Trotyl is a true nitro-compound, consisting of toluene as a nucleus, to which has been added by replacement of three hydrogen atoms, three NO_2 groups in a symmetrical arrangement. It can be made by the direct nitration of toluene with nitric acid, though in practice sulphuric acid is always used in addition to remove the water formed in the reaction.



The above gives an approximate representation of the nitration of toluene, which is given more fully in Fig. 18.1. It will be noticed that there is only one symmetrical trinitrotoluene; the other trinitrobodies, of which there are five in all, are known as the unsymmetrical T.N.Ts.

On detonation T.N.T. is converted into a mixture of gases.

The following figures, from Bichel, give the approximate composition of this mixture, the exact constitution of which will vary with the conditions under which detonation takes place.

	Per cent.
Carbon dioxide	3·7
Carbon monoxide	70·5
Nitrogen	19·9
Hydrogen	1·7
Carbon	4·2

The presence of free carbon suggests that T.N.T. is deficient in oxygen, and this is so. To supply this deficiency ammonium nitrate is added as an oxygen carrier in the amatols.

Manufacture of Trotyl

Before considering any processes in detail, it would seem desirable to view the nitration of toluene on a commercial scale in a more general manner.

When the war commenced in 1914, the nitration of toluene was little more than a laboratory operation, and it had not been established as a works process in government factories. The Research Department at Woolwich, by performing many hundreds of nitrations eventually established the best conditions for nitration, which were further confirmed by work on a small experimental plant with a capacity of ¼ ton of T.N.T.

Methods of nitration.

1. Direct nitration to T.N.T. in one stage.

This is a very wasteful method. As nitration proceeds, water is formed, and towards the end of the reaction, when the strongest acids are needed, all the water from the preceding stages of nitration has accumulated and dilutes the acids. To maintain the necessary concentration, a large excess of sulphuric acid or oleum is needed. This is expensive and also necessitates a very large plant to cope with this volume of acid.

2. Nitration in stages.

Three-stage. Toluene.........M.N.T..........D.N.T..........T.N.T.
Two-stage { Toluene.........M.N.T............................T.N.T.
Two-stage { Toluene...........................D.N.T..........T.N.T.

(*a*) Using fresh acid for each stage.

This is better than nitration in one stage, but the volume of acid required is still large. The process is uneconomical for another reason ; the lower nitro-compounds of toluene are very soluble in the nitrating acids, and this method does not permit of their recovery.

(*b*) Using the waste acids from the last stage for the earlier stages.

This is the most economical for the following reasons :

(i) The strongest acid is used in the final stage.

(ii) The waste acids contain nitro-compounds in solution as mentioned above (2(*a*)). These nitro-bodies are, however, more soluble in M.N.T. which extracts them from the waste acids and carries them forward to the next stage. This process is known as detoluation.

(iii) The quantity of acid required is reduced to a minimum, as the lower nitrations are easily carried out by the less concentrated acid.

In three-stage processes the manipulation of the acids is, usually, as follows :

The waste acid from stage 3 is fortified with nitric acid and used for stage 2 ; finally, the waste acid from stage 2 is diluted for stage 1.

The detoluation of waste acids is important. On the one hand, the recovery and further nitration of these nitro-bodies means an increased yield of T.N.T. from a given amount of toluene ; and, on the other hand, if permitted to pass away with the waste acids they cause a great deal of trouble by depositing in some part of the acid-recovery plant.

An important factor in the nitration of toluene is temperature. The following may be taken as representative of the temperature conditions in a typical three-stage process :

(i) Toluene to " Hypotol " (50 per cent. Toluene and 50 per cent. M.N.T.).

Carried out at about 20° C.

(ii) " Hypotol " to " Sesquitol " (25 per cent. M.N.T. and 75 per cent. D.N.T.).

Carried out at about 50° C.

(iii) " Sesquitol " to T.N.T.

Three hours at 70° C., one hour rising to 110° C., and finally, two hours at 110° C.

Washing of trinitrotoluene.

Originally, attempts were made to wash the acids from T.N.T. with soda, as in the manufacture of nitroglycerine. This proved absolutely impracticable as T.N.T. is attacked by alkali. The products of decomposition are dangerously sensitive.

The next development was the use of thorough and repeated washings with hot water. The disadvantage of this lay in the enormous quantities of water necessary to give satisfactory results ; as much as 5,000 gallons of water per ton of T.N.T. were needed.

Later, the pelleting of T.N.T. and the use of weakly alkaline salts such as sodium acetate reduced the amount of water needed to a reasonable amount. It must be remembered that the washing of T.N.T. is solely for the purpose of removing waste acids and inorganic impurities ; the removal of organic matter comes under the heading of purification.

Purification of T.N.T.

The organic impurities in crude T.N.T. are :

(i) Dinitrotoluene.
(ii) Unsymmetrical trinitrotoluenes.
(iii) Nitrobenzoic acids.
(iv) Nitrocresols.
(v) Tetranitromethane.

Of these only the first two are of importance. Nos. (iii) and (iv) are soluble in water and are usually removed in the washing processes ; No. (v) can also be removed by washing, though traces usually remain.

(i) Dinitrotoluene results from incomplete nitration, and is usually present in small quantities.

(ii) There are six isomeric trinitrotoluenes. Three are shown in Fig. 18.1, the remainder being unimportant. The two unsymmetrical T.N.Ts. shown, are known as β and γ T.N.T., which melt at 112° C. and 104° C. respectively. The elimination of isomers is of the greatest importance as exudation is due to their presence.

Exudation is the name given to the percolation of oily matter from the shell-filling into either the exploder system or through screw-threads to the exterior of the shell. This oily matter is a mixture of the unsymmetrical isomers of T.N.T. and the traces of D.N.T. present. Such a mixture has a low melting-point, so that it is liquid at temperatures of storage such as may obtain in the tropics.

This is undesirable for two reasons :

(i) The exuded matter is explosive, and is therefore a source of danger, if it gains access to a position where it may be subjected to shock or friction, *e.g.* in the screw-threads of shell.

(ii) If the exploder system is not contained in a steel container, the exudation products may saturate the substances in the system and impair its efficiency. For this reason C.E., being less affected, is always used instead of trotyl for exploder systems for use in the tropics.

Two methods of eliminating the unsymmetrical T.N.Ts. deserve consideration :

1. The sodium-sulphite process.
2. The removal of meta-nitrotoluene.

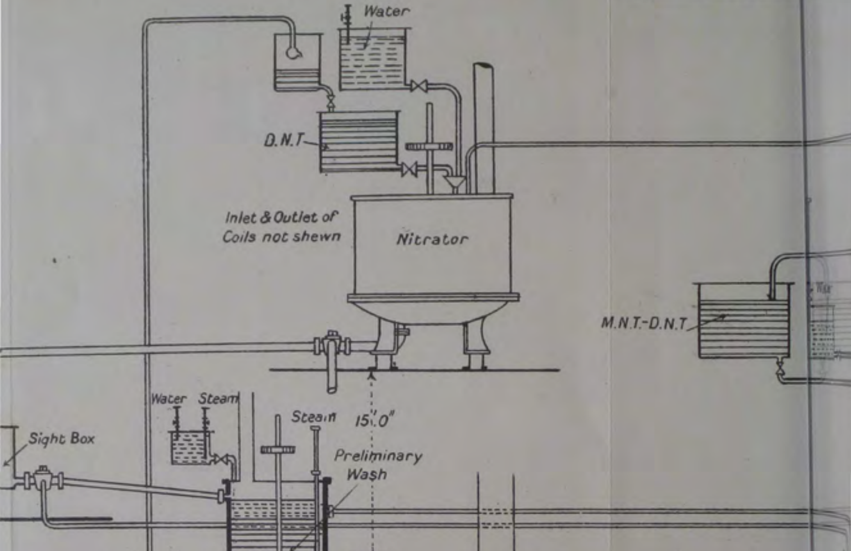
1. The sodium-sulphite process.

This method of purification was evolved by the French in 1916 and was widely adopted in this country.

The crystals of T.N.T. are treated with a 10 per cent. solution of sodium sulphite (Na_2SO_3) at a temperature of 35–45° C. The sodium sulphite is formed as a by-product in the manufacture of "synthetic" phenol—by the Sutton Oak process, Chapter VIII. Interaction between the sulphite and the unsymmetrical isomers

DIAGRAMMATIC SECTION OF ONE

APPROXIMATE



FIG

NIT T.N.T. NITRATION PROCESS.

CALE 3/16 IN. = 1 FT.

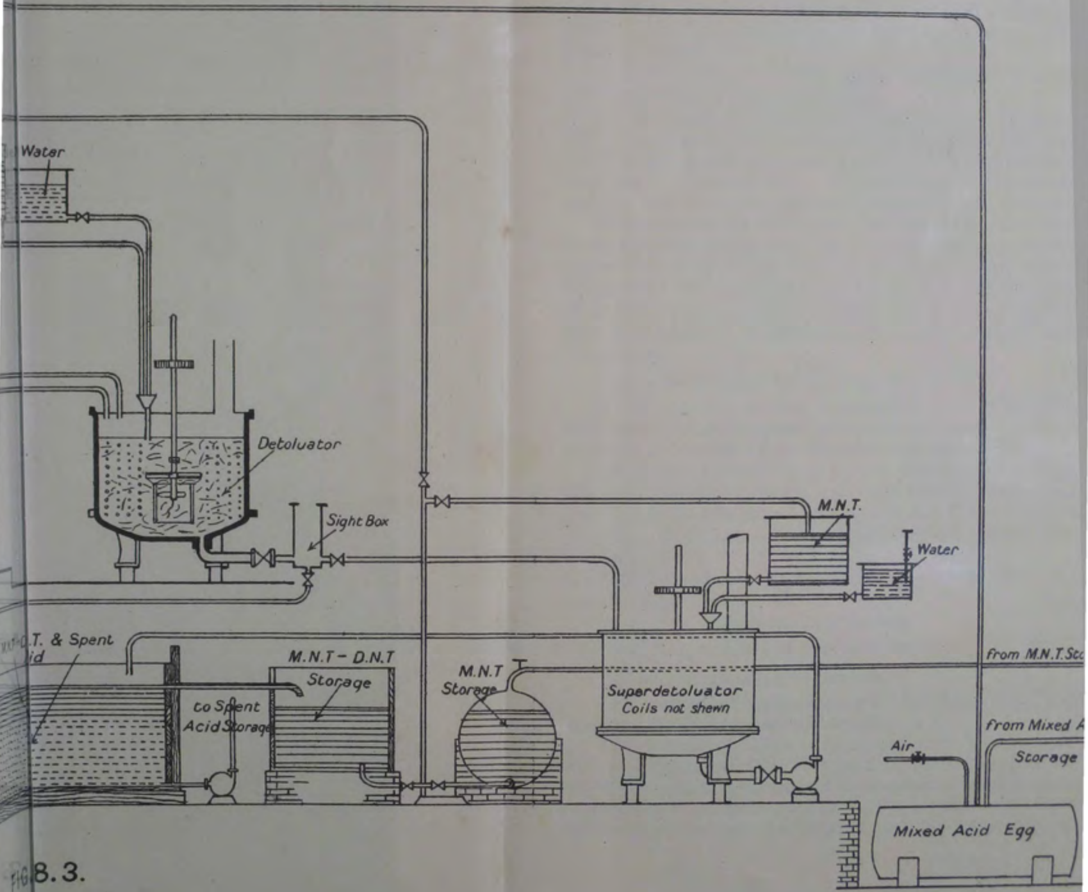


FIG 8.3.

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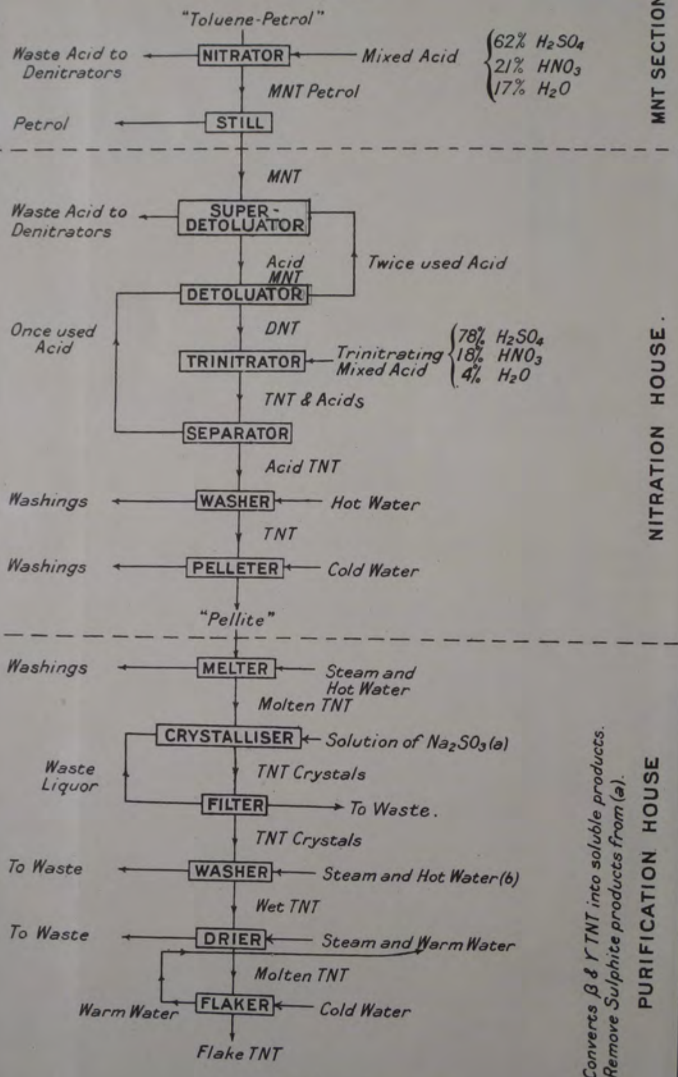
FLOW DIAGRAM FOR QUEENSFERRY PROCESS.
(T.N.T)



(a) Converts β & γ TNT into soluble products.
(b) Remove Sulphite products from (a).

FIG. 18·2

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results in the formation of salts which are readily soluble in water. Subsequent washing with water removes these salts in the form of a deep blood-red solution.

It should be noted that this method does not remove dinitrotoluene. Re-crystallization of the T.N.T. from a hot alcohol solution will give a purer product; washing with cold alcohol is also efficacious.

x

Page 133. *After* line 7 *insert* :—

x — In a more recent patented modification of the sulphite purification process, as worked at Irvine, molten T.N.T. is treated with a hot aqueous solution of sodium sulphite and boric acid. The liquids are allowed to settle, the aqueous layer run away and the purified T.N.T. washed with hot water until free from red colour. These operations are all carried out in the same vessel as is used for washing the crude T.N.T. free from mineral acid. The washed molten T.N.T. is then treated as described on page 135 (3 (iv)). aml

Fig. 18.2 gives a flow diagram of this process. It is divided into three parts.

1. The M.N.T. Section.

(i) The "toluene-benzene," as received from overseas, is nitrated, using a mixed acid consisting of 62 per cent. sulphuric acid, 21 per cent. nitric acid, and 17 per cent. water. This converts the toluene into M.N.T., while the remainder of the "toluene-benzene," which consists of cyclo-paraffins, is unaffected by the acids.

(ii) The product is known as "M.N.T.-petrol." The M.N.T. is separated by fractional distillation, and is conveyed by pipe line to the T.N.T. section.

2. The T.N.T. Section. (*See* Fig. 18.3.)

(i) The M.N.T. is treated in a "super-detoluator," which is similar in design to a nitrator, using waste acids from previous operations. The reasons for this step will be apparent from the foregoing.

(ii) The "Acid M.N.T." from (i) now undergoes nitration in a "detoluator," where it is partially converted to D.N.T. The acid used is waste acid from the final stage of nitration.

(iii) The nitration of the D.N.T. to T.N.T. is finally completed by the use of a mixed acid consisting of 78 per cent. sulphuric acid, 18 per cent. nitric acid, and 4 per cent. water. A section through a nitrator is given in Fig. 18.4.

(iv) The T.N.T. and waste acids are run into a separator, the acid going back as once-used acid to stage (ii), and the T.N.T. to a washer. At this point the T.N.T. is molten and it is washed by agitation with boiling water. The washings go to waste and the T.N.T. to the pelleting tank.

FLOW DIAGRAM FOR QUEENSFERRY PROCESS.
(T.N.T)

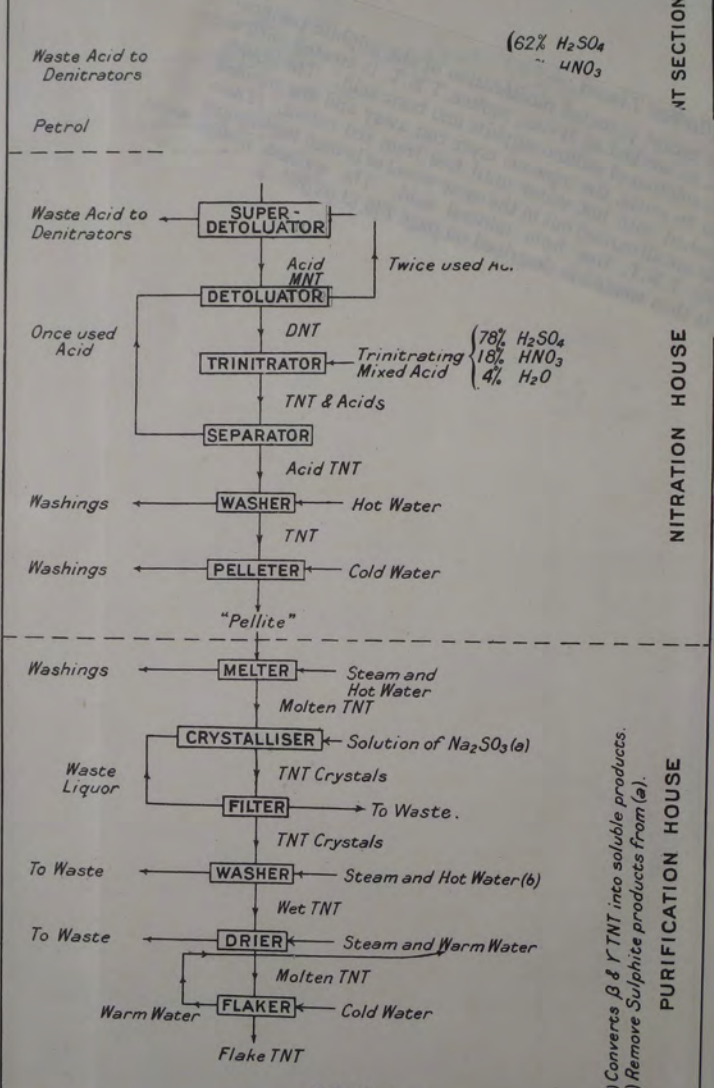

FIG. 18·2

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results in the formation of salts which are readily soluble in water. Subsequent washing with water removes these salts in the form of a deep blood-red solution.

It should be noted that this method does not remove dinitrotoluene. Re-crystallization of the T.N.T. from a hot alcohol solution will give a purer product; washing with cold alcohol is also efficacious.

x

2. A reference to Fig. 18.1 will show that the unsymmetrical T.N.Ts. are derived from meta-nitrotoluene. If this can be removed before proceeding further with the nitration, the undesirable isomers will not be formed. A process whereby meta-nitrotoluene was removed by fractional distillation was developed at Oldbury during the latter part of the Great War, and gave the most promising results, but it had hardly left the experimental stage when the War ended.

The Queensferry discontinuous process for manufacturing T.N.T.

Fig. 18.2 gives a flow diagram of this process. It is divided into three parts.

1. The M.N.T. Section.

(i) The "toluene-benzene," as received from overseas, is nitrated, using a mixed acid consisting of 62 per cent. sulphuric acid, 21 per cent. nitric acid, and 17 per cent. water. This converts the toluene into M.N.T., while the remainder of the "toluene-benzene," which consists of cyclo-paraffins, is unaffected by the acids.

(ii) The product is known as "M.N.T.-petrol." The M.N.T. is separated by fractional distillation, and is conveyed by pipe line to the T.N.T. section.

2. The T.N.T. Section. (*See* Fig. 18.3.)

(i) The M.N.T. is treated in a "super-detoluator," which is similar in design to a nitrator, using waste acids from previous operations. The reasons for this step will be apparent from the foregoing.

(ii) The "Acid M.N.T." from (i) now undergoes nitration in a "detoluator," where it is partially converted to D.N.T. The acid used is waste acid from the final stage of nitration.

(iii) The nitration of the D.N.T. to T.N.T. is finally completed by the use of a mixed acid consisting of 78 per cent. sulphuric acid, 18 per cent. nitric acid, and 4 per cent. water. A section through a nitrator is given in Fig. 18.4.

(iv) The T.N.T. and waste acids are run into a separator, the acid going back as once-used acid to stage (ii), and the T.N.T. to a washer. At this point the T.N.T. is molten and it is washed by agitation with boiling water. The washings go to waste and the T.N.T. to the pelleting tank.

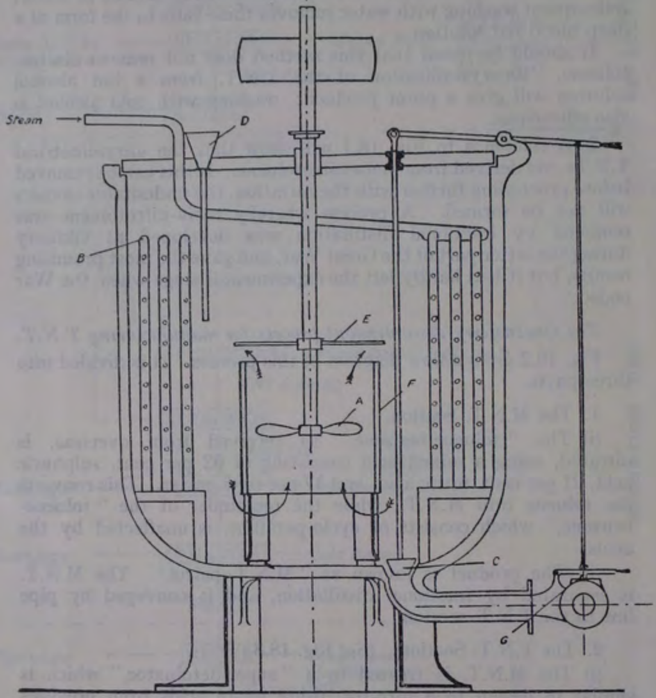

FIG. 18.4.

SECTION THROUGH A TOLUENE NITRATOR.

The vessel as a whole is made of cast-iron. It is fitted with coils (B) into which steam or water can be admitted, according as it is desired to raise or lower the temperature in the vessel.

The D.N.T. and mixed acids are introduced through the orifice (D). (A) is the stirrer. It consists of a paddle (like a two-bladed propeller) operated by a belt-driven shaft. The paddle revolves inside a vertical cylinder (F), and causes the liquids to circulate in the manner indicated by the arrows. As the liquids rise from the cylinder they meet the disrupter (E). This consists of two flat blades, attached to the same shaft as the stirrer, which come into violent contact with the rising fluids and ensure the admixture of the constituents, so that nitration proceeds as rapidly and as thoroughly as possible.

(C) is the delivery valve, and (G) the valve into the main delivery pipe. The two valves are connected together as shown, so that (C) cannot be opened unless (G) also is opened.

T. N.T. F

DIAGRAMMATIC SECTION OF SULPH
COURSE OF T.N.T. FROM PELLI

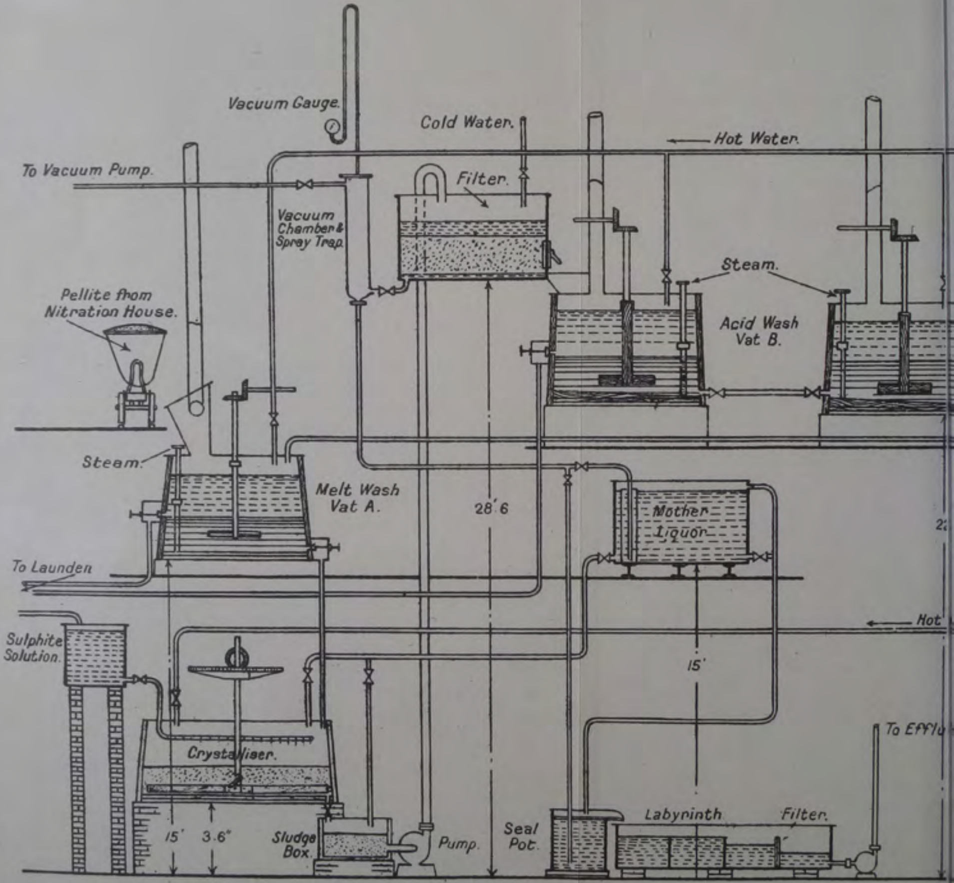

FIG. 1

ANT.
PURIFICATION HOUSE, SHEWING
TO FINISHED PRODUCT.

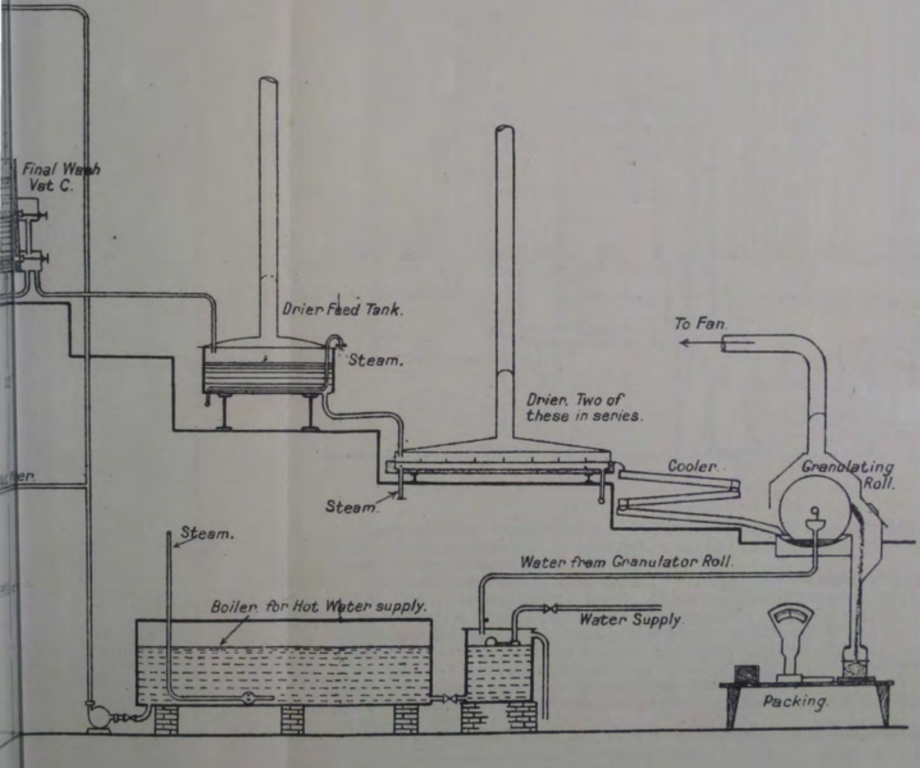

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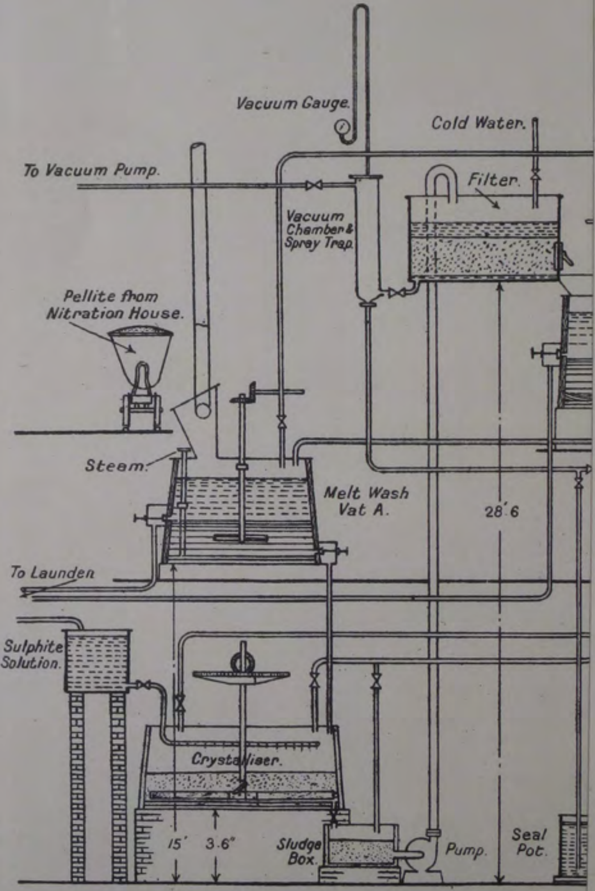
DIAGRAM



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(v) The molten T.N.T. as it runs into the pelleter is met by a jet of cold water. This immediately solidifies the T.N.T., which is broken up by the force of the jets into small granules or pellets. In this form it is known as " pellite " and is in a suitable condition for transport to the adjoining purification plant.

3. *The Purification House.* (*See* Fig. 18.5.)

(i) The " pellite " is melted under the action of steam and hot water, which also serves as an additional washing.

(ii) The molten T.N.T. is then cooled in a " crystallizer " and washed with a solution of sodium sulphite (Na_2SO_3) and waste liquor from the next operation. This step has already received attention in the preliminary notes on the manufacture of T.N.T.

(iii) The T.N.T. crystals are filtered from the sulphite solution and pass on to a washer, where they are subjected to steam and hot water.

(iv) The wet T.N.T. is dried by steam heat and melted. In this condition it passes into a steam-jacketed trough. Revolving in this trough, and partially immersed in the molten T.N.T. is a gunmetal drum. This drum is internally cooled by water, which enters through one of the trunnions supporting it, and overflows through the other. The drum rotates at about 8 revolutions per minute, and in so doing picks up molten T.N.T., which solidifies in a thin film on the periphery of the drum. A metal scraper removes this T.N.T. in the form of flakes, which pass away down a chute to the packing room on the floor below.

The counter-current washing of T.N.T.

This was introduced at a later period than the process described above. The plant consists of about nine pairs of pots ; one vessel of each pair is fitted with a stirrer and is known as the agitator, the other vessel of the pair being known as the settler.

Clean water and molten T.N.T. pass in at opposite ends of the plant and proceed in contrary directions emerging as neutral T.N.T. and strongly acid water.

The Oldbury continuous process for manufacturing T.N.T.

This is a counter-current process. It is carried out in units, each unit consisting of three nitrators and three settlers, arranged in pairs and connected together, as shown in Fig. 18.6.

Strong sulphuric acid and M.N.T. (made separately as in the Queensferry process) are introduced at opposite ends of the plant, and the nitric acid is introduced into the nitrators direct as shown. The effluent products are T.N.T. and spent acid.

A pair of pots consists of a nitrator and a settler, the former being fitted with a stirrer. From a settler, the nitro-body goes forward to the next nitrator, and the acids travel in the opposite direction. Thus the nitration is carried out by acid that is progressively stronger as the nitration approaches completion.

The temperature is never allowed to exceed 100° C., the necessary control being provided by steam and water coils.

This plant was wonderfully efficient. That at Oldbury was built to give 100 tons of T.N.T. a week, but 500 tons was often produced within this period.

The further purification of the T.N.T. is carried out as at Queensferry.

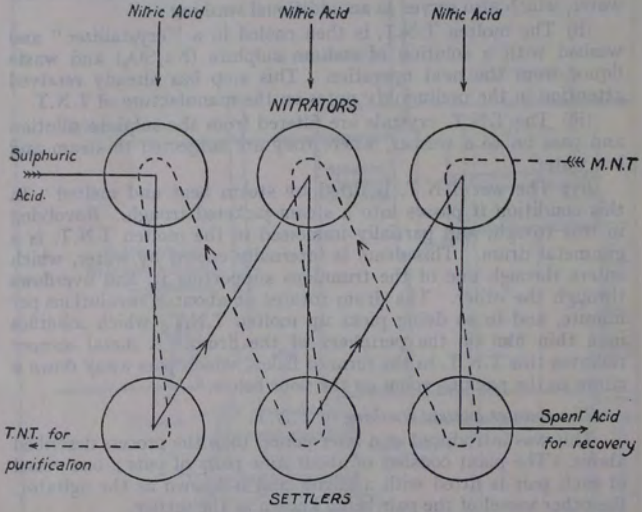


FIG. 18.6.—Diagram of the Oldbury Continuous Process for the nitration

Page 136. *Below* Fig. 18.6 *insert* :—

The counter-current process, as worked at Irvine, embodies the following features :—

(i) The amount of T.N.T. in the plant is small.

(ii) The transfer of the acid and of the T.N.T. is positive and controllable.

(iii) The flow of liquid is visible.

am 1

(iv) The separators used are shallow, and special weirs are employed.

houses), thorough ventilation, and, in processes where T.N.T. dust is prevalent, the use of respirators.

T.N.T. is not easy to detonate, but with suitable initiation this can be done, giving a very powerful detonation, having a velocity of 6,950 metres/second.

It is very stable in storage, and relatively insensitive to shock and friction; operations such as milling and crushing can be carried out with little risk, using plant of suitable design under clean conditions.

When toluene is nitrated, about 5 per cent. of the final product, under the usual conditions of nitration, is composed of the unsymmetrical isomers referred to earlier in this chapter. A comparison of their properties with those of symmetrical T.N.T. is given in the table below.

	Properties of T.N.T.	Properties of the Unsymmetrical Trinitrotoluenes
1. Stability ...	Very good	Fair
2. Activity ...	Reactive with alkalies to form objectionable compounds	Reactive with alkalies to form objectionable compounds
3. Sensitivity ...	Very insensitive	More sensitive than T.N.T.
4. Solubility ...	Practically nil in water. Very soluble in organic solvents	Similar to T.N.T. Forms soluble salts with Na_2SO_3
5. Melting-point	81·5° C.	104°–112° C. (refers to β and γ T.N.T. respectively)

T.N.T. is divided into three grades for service purposes. The chief characteristics of these grades are given below.

Trotyl (Grade 1)

Melting-point. Not below 80° C.

Stability. Good. Decomposition is very slow at 140° C. Practically non-reactive.

Figure of insensitiveness. 115. (Picric acid=100.)

Toxic properties. Poisonous both internally and to the skin.

More difficult to detonate than lyddite.

Suitable for all purposes.

Trotyl (Grade 2)

Melting-point. Not below 79·5° C.

Less pure than Grade 1.

Other properties are similar to Grade 1.

Used in the amatols, etc.

Liable to exude slightly in warm storage.

Trotyl (Grade 3)

Melting-point. Not below 76° C.

Stability. Almost as good as Grade 1.

Insensitiveness. A little more sensitive than Grade 1.

The temperature is never allowed to exceed 100° C., the necessary control being provided by steam and water coils.

This plant was wonderfully efficient. That at Oldbury was built to give 100 tons of T.N.T. a week, but 500 tons was often produced within this period.

The further purification of the T.N.T. is carried out as at Queensferry.

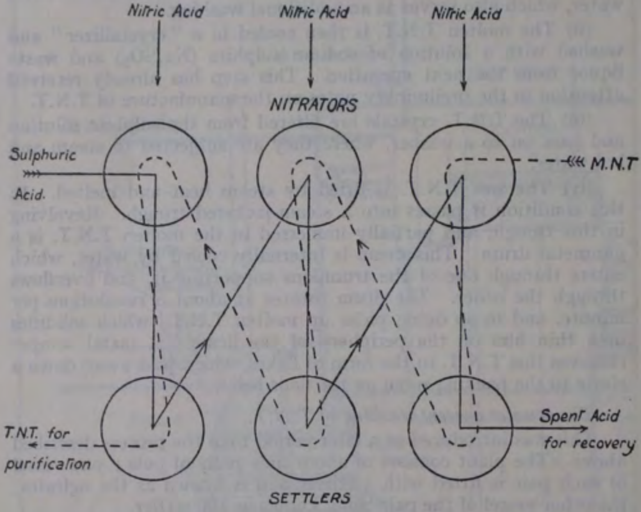


FIG. 18.6.—Diagram of the Oldbury Continuous Process for the nitration of Toluene to T.N.T.

Properties and Uses of T.N.T.

Symmetrical trinitrotoluene is a pale yellow crystalline solid melting at 81° C. It is practically insoluble in water, but is readily dissolved by most organic solvents, especially ethyl acetate and acetone.

It is poisonous. In T.N.T. factories, careful attention must be paid to cleanliness (adequate provision of baths and wash-houses), thorough ventilation, and, in processes where T.N.T. dust is prevalent, the use of respirators.

T.N.T. is not easy to detonate, but with suitable initiation this can be done, giving a very powerful detonation, having a velocity of 6,950 metres/second.

It is very stable in storage, and relatively insensitive to shock and friction; operations such as milling and crushing can be carried out with little risk, using plant of suitable design under clean conditions.

When toluene is nitrated, about 5 per cent. of the final product, under the usual conditions of nitration, is composed of the unsymmetrical isomers referred to earlier in this chapter. A comparison of their properties with those of symmetrical T.N.T. is given in the table below.

	Properties of T.N.T.	Properties of the Unsymmetrical Trinitrotoluenes
1. Stability ...	Very good	Fair
2. Activity ...	Reactive with alkalies to form objectionable compounds	Reactive with alkalies to form objectionable compounds
3. Sensitivity ...	Very insensitive	More sensitive than T.N.T.
4. Solubility ...	Practically nil in water. Very soluble in organic solvents	Similar to T.N.T. Forms soluble salts with Na_2SO_3
5. Melting-point	81·5° C.	104°–112° C. (refers to β and γ T.N.T. respectively)

T.N.T. is divided into three grades for service purposes. The chief characteristics of these grades are given below.

Trotyl (Grade 1)

Melting-point. Not below 80° C.

Stability. Good. Decomposition is very slow at 140° C. Practically non-reactive.

Figure of insensitiveness. 115. (Picric acid=100.)

Toxic properties. Poisonous both internally and to the skin.

More difficult to detonate than lyddite.

Suitable for all purposes.

Trotyl (Grade 2)

5° C.

Stability.

Insensitiveness. A

Slightly less powerful than pure trotyl, and more poisonous.

Very liable to exudation.

If a melting-point of 78° C. is used instead of that given above, the detonation is as good as with other grades. The detonation becomes inferior with a lower melting-point, on account of the presence of dinitrotoluene.

This grade is practically obsolete for military purposes.

The tests applied to T.N.T. for acceptance and grading are five in number. (C.W.D. Specifications. Nos. 704–708 give exact details.)

1. *Setting-point test* (*or melting-point*).

The reasons for this are obvious from the foregoing.

2. *Volatile matter.*

This test is an indication of the presence of moisture or solvents.

3. *Ash content.*

The percentage of inorganic impurities, *e.g.* grit, lead or iron salts of the nitrating acids, is given by this test.

4. *Acidity.*

This test ensures freedom from waste acids, which may be present if the washing is insufficient.

5. *Percentage insoluble in benzene.*

In the manufacture of T.N.T. a product known as " transformation product " is formed. This has been traced to interaction between alkaline material (such as lime in water) and T.N.T., and affects stability adversely. A check on the amount present is imposed by this test.

Trinitrotoluene can be used for many different purposes in the Service. It is not proposed to enter into any details of its service uses in this book, as these can be obtained from the Text Book of Ammunition (1936).

As a shell filling, T.N.T. is often used alone, but it is more usually mixed with ammonium nitrate in the amatols. These mixtures not only have good explosive properties, but are a great economy as ammonium nitrate is cheap in comparison with T.N.T.

Amatol

Amatol is an intimate mixture of ammonium nitrate and trotyl. It was proposed with the object of economizing in trotyl, and at the same time taking advantage of the excess of oxygen possessed by ammonium nitrate to compensate partially or completely for the deficit of oxygen in T.N.T.

There are many of these mixtures which differ only in the proportion in which the two constituents are present. The constitution of any one of these mixtures is given by its name ; thus " Amatol 80/20 " denotes a mixture of 80 per cent. ammonium nitrate with 20 per cent. T.N.T.; the first number always refers to the percentage of ammonium nitrate. The amatols in use range from 40/60 to 80/20; other proportions that have been used are 45/55, 50/50, 83/17, and 90/10. Amatol is known in Germany as Fullpulver, and is designated Fp. 60/40, 20/80, etc., the numerators of the fractions referring to the percentage of T.N.T. present.

The methods of manufacturing and filling shell with amatol differ with the composition of the particular amatol. The various methods are summarized in Table 18.A.

AMATOL 40/60

General properties.

Melting-point. About 76° C., corresponding to the melting-point of the T.N.T. used.

Stability and exudation. Satisfactory if the ingredients are pure.

Figure of insensitiveness. 115. (Picric acid=100.)

Toxic properties. Poisonous owing to T.N.T. Care should be taken in handling and to avoid inhaling vapour.

Detonation. Good. Velocity 6,470 m/s.

Method of filling. T.N.T. is melted and powdered ammonium nitrate added; the whole is stirred to form a mass of the consistency of porridge. The shell are filled by pouring.

Amatol 80/20

General properties.

Melting-point. Not readily fusible, but softens at the melting-point of T.N.T. Advantage is taken of this in the " semi-melt " method of filling of hot mixed amatol.

Stability. Good with pure ingredients.

Figure of insensitiveness. 115. (Picric acid=100.)

Toxic properties. Slightly poisonous owing to the T.N.T.

Detonation. Very powerful when properly initiated. Velocity 5,080 m/s.

Shells are filled either by hand-stemming the cold amatol and consolidating it by mechanical plungers, or, with hot-mixed amatol, the hot plastic mass is compressed direct into the shell by hand or by screw-filling machine.

As combustion is complete with this filling, very little smoke is formed on burst, so a smoke mixture is usually provided, to assist observation.

Amatol 80/20 is practically the only amatol at present in use in the Service. For shell-filling purposes recent trials have indicated the need for a greater proportion of T.N.T. than 20 per cent., with a view to improved performance, and superior results have been established for amatols of 70/30 and 60/40 proportions. It

Table 18.A

AMATOL SHELL FILLING

Composition	Method of mixing	Method of Filling	Appearance of Burst	Remarks
80/20	(*a*) Cold milling in an edge-runner mill	(i) Hand stemming (ii) Screw filling } followed by press plunger for consolidation	Contains sufficient oxygen for complete combustion and therefore practically no smoke. A smoke mixture is provided to assist observation	Charges may shrink slightly and become loose
	(*b*) Hot mixing in a steam-jacketed pan *	(i) Hand stemming (ii) Screw filling } Consolidation with press-plunger not necessary		Hot-mixed charges do not shrink
40/60	Hot mixing *	When hot is fluid and therefore poured	Deficient in oxygen and gives some smoke on burst	These amatols are easy to mix and fill, but the process is less rapid than pressing or screw filling as applied to 80/20
50/50	Hot mixing *	do.	do	50/50 is less easy to pour than 40/60

* Hot mixing is carried out at 85-95° C.

has been decided to use 60/40 amatol (coldpressed) as the war-time filling for the 25-pr. gun, provided sufficient T.N.T. is available.

Fumyl

A mixed explosive similar to amatol has been used for the smoke mixture and bursting charge in chemical shell. It is known as fumyl, and has the following composition :

Trotyl Grade 2	45
Ammonium chloride	40
Ammonium nitrate	15

Baratol

Mixtures of barium nitrate and T.N.T. find some application in the Services.

Weight for weight baratol is inferior to amatol as a bursting charge, but volume for volume gives comparable results. There are difficulties in applying it for shell filling however, on account of its high density.

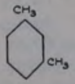
Baratol has the advantage over T.N.T. and ammonium nitrate explosives that it retains its sensitiveness to small impulses (*e.g.* from a No. 6 detonator) after prolonged warm storage. For this reason a 20/80 cold mixed baratol is used as a filling for hand grenades.

A small proportion of barium nitrate is also useful in assisting cast T.N.T. to maintain detonation under inadequate confinement, *e.g.* in anti-tank mines.

Unlike ammonium nitrate, barium nitrate is not water-seeking and does not attack copper or its alloys.

Trinitroxylene

Trinitroxylene is similar to T.N.T., and is made by the direct nitration of xylene. It has been tried as an alternative to T.N.T. as an additional source of supply. There are several trinitroxylenes, but symmetrical trinitro-meta-xylene, is the only one of importance as an explosive. It melts at 182° C. and detonates with a maximum velocity of 6,600 m/s.



Meta Xylene.

Dinitrotoluene

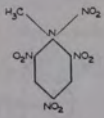
This compound can be made by direct nitration as suggested in the three-stage processes for the nitration of toluene described in the early part of this chapter. It is an insensitive crystalline solid melting at 65° C. It is used as a moderant in " Dupont Powder ". Dupont powder is a nitrocellulose powder, which is coated with dinitrotoluene. The powder is in the form of very small lengths of thin tube. In the final stages of its manufacture it is immersed in a solution of D.N.T. in alcohol, followed by evaporation of the solvent. This leaves a coating of D.N.T. on the grains of powder. It serves the purpose of retarding (or moderating) the rate of burning, which prevents (i) a too rapid rise of pressure ; and (ii) a rapid fall from the maximum pressure once it is attained.

CHAPTER XIX

TETRYL, OR COMPOSITION EXPLODING

Introduction.

This is a single chemical compound, trinitro-phenyl-methyl-nitramine, and is commonly known in the Service as " C.E." It is a true nitro-compound, and was discovered by Mertens in 1877. It was introduced as an intermediary several years before the Great War, and has now become of great importance in this capacity Its chemical constitution is :



Its stability is lowered by picric acid, and for this reason it is not used as an exploder in lyddite shell ; it is unaffected by exudation from T.N.T., but is readily decomposed by alkalies. It contains more nitro-groups, and so a higher oxygen content, than either picric acid, or T.N.T., and probably for this reason is more readily ignited, or initiated to complete detonation than these.

The manufacture of tetryl in this country is carried out by the nitration of dimethyl aniline, which is not itself made at the explosive factories.

Dimethyl aniline may be prepared by a variety of reactions :

(*a*) 80 parts by weight of aniline, 78 parts of methyl alcohol, which must be free from acetone, and 8 parts of 96 per cent. sulphuric acid, are heated to 230° C. in an autoclave ; if the above quantities are in kilograms, the reaction takes about 11 hours. The contents of the autoclave are allowed to cool, and on opening the safety valve there is a large escape of gas containing methyl ether. The liquid from the autoclave is neutralized with caustic soda, and steam distilled. There is a yield of about 98 parts by weight of dimethyl aniline, this being about 94 per cent. of the yield given by theory.

(*b*) Aniline and milk of lime are placed in an autoclave, and methyl chloride gas is pumped in at a pressure of five or six atmospheres, the temperature being 100° C. The final product is obtained by steam distillation as before.

The base dimethyl aniline is insoluble in water, and reacts very violently in contact with nitric acid. For the manufacture of tetryl it is first converted into the soluble sulphate. Dimethyl aniline sulphate dissolved in sulphuric acid is added to nitric acid, resulting in a mixture of crude tetryl with a very small proportion of tetranitro-phenyl-methyl-nitramine. This is an unstable by-product containing an extra nitro-group ; it is readily hydrolyzed to hydroxy tetryl and ~~nitric~~ nitrous acid by prolonged boiling in water, provided that it is not present in a greater proportion than 1 to 2 per cent. As any by-products from the boiling are soluble, they are removed in the washings. The temperatures of the various processes of manufacture, and the strengths and proportions of the nitrating acids are calculated :

(i) To keep down the proportion of tetra-nitro-phenyl-methyl-nitramine formed to 1 or 2 per cent.

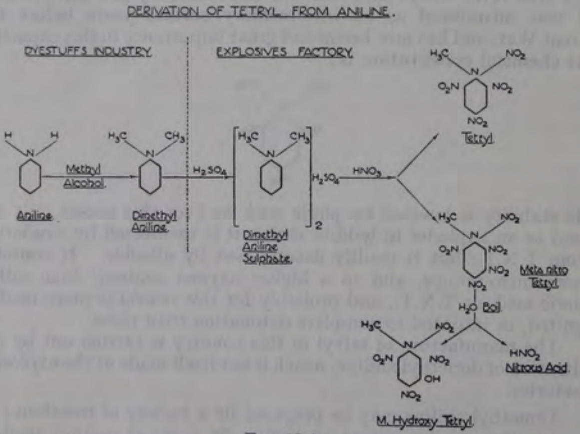


FIG. 19.1.

(ii) To ensure that the nitration is rapid enough to prevent the locking up of unnitrated material in the tetryl crystals that are formed.

The chemical processes of manufacture may be summarized as in Fig. 19.1.

Manufacture

The manufacture of tetryl may be divided into two main stages :

1. The nitration of dimethyl aniline.
2. The purification of the crude tetryl thus obtained.

The following is an outline of the manufacturing process as carried out at Royal Gunpowder Factory, Waltham Abbey.

1,500 lb. of 94 per cent. sulphuric acid, and 800 lb. of 90 per cent. nitric acid are used to sulphate and nitrate 96 lb. of dimethyl aniline. It is found that a large excess of acid minimizes the risk of fire in the nitrating vessel.

1. *The nitration of dimethyl aniline.*

This is best considered in its several different stages.

(*a*) *Sulphation.* This is carried out in a cast-iron pot fitted with cooling coils and stirring gear. Dimethyl aniline is poured into the sulphuric acid in the pot through a regulated feed. The temperature is controlled by the regulation of the feed, and is not allowed to rise above about 30° C. lest charring and violent fuming should set in. The solution is finally cooled to about 15° C.

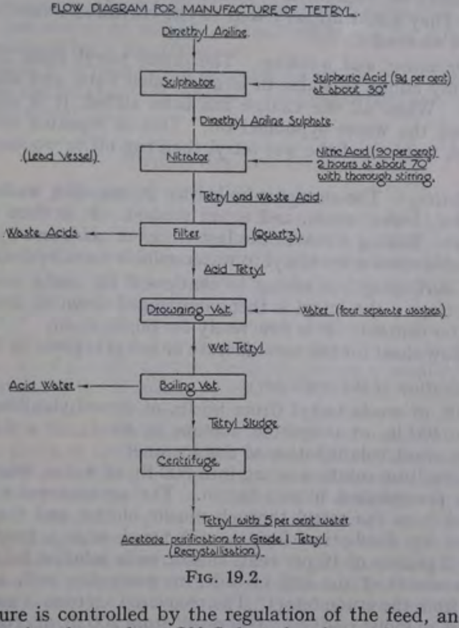


FIG. 19.2.

(*b*) *Nitration.* This takes place in lead pots, which are fitted with hot and cold water coils. The charge of nitric acid in the pot is heated to about 45° C. by means of the hot-water coil, and the cold-water coil is then put into operation. The dimethyl aniline sulphate is run in, the temperature being allowed to rise gradually, until it reaches 70° C. By varying the inlet flow the contents are kept at this temperature. The nitration is rather violent, and care is necessary to prevent the charge catching fire. After nitration the contents of the pot are cooled to about 30° C. and run on to the filters. Nitration occupies about two hours.

(*c*) *Filtration.* The charge is filtered through graded quartz, supported on lead quadrants. This method is by no means ideal, as much of the C.E. passes through the filter with the waste acid. The waste acid, therefore, has to be run into lead settling tanks, crude C.E. separating out on the surface of the acid, and being skimmed off periodically. Owing to the inefficiency of the quartz filters, filters of " staybrite " gauze are being tried at Waltham Abbey. They stand up very well to the corrosive waste acid, and should be successful.

(*d*) *Drowning and washing.* The crude tetryl from the filters is gradually added to water in large wooden vats, and thoroughly agitated. When all the charge has been added, it is allowed to settle, and the water syphoned off. This is repeated four times with fresh water, and the wet tetryl then run off to wooden boiling vats.

(*e*) *Boiling.* The charge is boiled for 20 minutes, washed twice with water, boiled again, and again washed. It is then run to a centrifuge. Boiling removes the last traces of acid, and hydrolyzes the unstable meta-nitro-tetryl to water-soluble meta hydroxy tetryl.

(*f*) *Centrifuging.* Washing is continued for some minutes in the centrifuge ; the tetryl is then centrifuged down to about 5 per cent. water content. It is now ready for purification.

The flow sheet for the manufacture of tetryl is given in Fig. 19.2.

Purification of the crude tetryl.

200 lb. of crude tetryl (from 96 lb. of dimethylaniline) is dissolved in 400 lb. of anhydrous acetone at 40° C., in a closed iron pot (to prevent volatilization of the acetone).

The resulting solution is run into 300 lb. of water, whereby the tetryl is precipitated from solution. The acetone-water mixture is filtered from the tetryl through muslin cloths, and the acetone recovered by distillation from a still fitted with a fractionating column, 2 gallons of 10 per cent. caustic soda solution being added to the contents of the still in order to neutralize such acid as is derived from the crude tetryl. The recovered acetone is used again.

173 lb. of moist purified tetryl result from 200 lb. of crude tetryl.

The tetryl is now dried on trays in air ovens at 80° C. for 40 hours. It is then sieved. The pure tetryl is now sent off to the Corning Process.

147 lb. of pure C.E. result from 96 lb. of dimethyl aniline (yield 65 per cent. of theory).

Corning of pure tetryl.

Tetryl dust is poisonous, and causes dermatitis. In order to overcome this difficulty, the pure C.E. is corned.

The pure C.E. is incorporated, 100 lb. at a time, with 1 lb. of gum arabic, which has been dissolved in 3 litres (about 5 pints) of distilled water. The incorporating machines are of the same type as those used for cordite. There is no definite time laid down for incorporation but, if too long a time elapses before stirring, the mixture takes up water more thoroughly and is harder to dry. The corned C.E. is now dried at 90° C. for 3 days until it contains less than 2 per cent. of water. The corned C.E. is now sieved and bagged, the dust which passes the sieve being re-corned.

The resulting corned C.E. must contain not more than 1·25 per cent. of gum arabic by weight and must all pass a No. 8 G.S. sieve, but be retained by a No. 100 sieve.

Corned C.E. is used for all purposes for which C.E. is applicable, except for the fire channels of fuzes ; for this purpose only uncorned C.E. is at present used.

Properties and Uses

C.E. is a pale yellow crystalline substance. It is soluble in acetone, benzene, etc., but is insoluble in water and is not hygroscopic. It melts at 129° C. and readily inflames. It is not used in the cast condition, but is made into pellets by compression, and is also used, tightly packed, as powder. Its apparent density when compressed into pellets is about 1·5.

Its chief use is as an intermediary between main explosive charges and their initiating fulminate detonators. As it has a higher degree of sensitivity than the main charge, it readily responds to the impulse of the initiator, whilst the violence of its own detonation ensures that of the main charge. At the same time it is much less sensitive than mercuric fulminate, and can itself safely withstand the shock of discharge, when used as a fuze filling.

It is used as a filling for the magazines of detonating fuses and gaines, for exploder systems in shells, and in composite detonators, etc. ; *i.e.* in general, to reinforce the initiating impulse from a detonating composition which can only be used with safety in such small quantities that it would not serve to initiate the main charge to complete detonation without the assistance of an intermediary.

Grades 1 and 1a are used for all purposes for which C.E. is applicable. Grade 2 is used for exploders only.

Its cost and high sensitivity preclude C.E. from use as a shell filling. (The figure of insensitiveness of C.E. is 70, where Picric Acid is 100.) It cannot be safely melted and cast in any quantity. When suitably initiated its detonation is very violent ; and the velocity of detonation is high (7,520 metres per second).

CHAPTER XX

MIXED EXPLOSIVES

Introduction.

In addition to the high explosives already mentioned, there are a large number of explosive mixtures which can be detonated, and which are largely used for such purposes as mining operations, demolitions, and trench warfare (fillings for bombs and grenades). For the former, mixtures with a high oxygen content which form no poisonous gases on detonation are often necessary; whilst bombs and grenades may be filled with high explosives which are too sensitive, or in other ways unsuitable, for shell fillings, so freeing material for the latter purpose, and furthering economy by making use of the cheapest available material.

In war, the demand for explosives is likely to exceed the supply, and it becomes necessary to take advantage of any explosive material that is available. Many mixtures are thus used in war that find no place in the Service in times of peace. A short "Dictionary of Explosives" for reference is included in Appendix IV, which is not entirely confined to explosives used in the Service in peace time.

The general principle of mixing explosives, is to obtain the maximum total energy from the mixture by providing sufficient oxygen completely to oxidize all the combustible material in it.

The most suitable oxidizing agents which can be readily and economically made, are the nitrates, chlorates, and perchlorates, of sodium, potassium, and ammonium.

Synthetic and other methods of ammonia supply, the oxidation of ammonia to nitric acid, and the production of ammonium nitrate have been considered in Chapter IX.

Other intermediates and explosives, which form ingredients of the explosives to be described in this chapter, have already been described as follows:

(i) Chlorates and perchlorates in Chapter XI.
(ii) Nitroglycerine in Chapter XII.
(iii) Nitrocellulose and guncotton in Chapter XIII.

Dynamites.

This has become a generic name for a class of explosive in which nitroglycerine is the main active constituent. The first dynamite was suggested by Nobel in 1866. He found that the infusorial earth "kieselguhr", after calcination, which drove off moisture and organic matter, would absorb about three times its own weight of nitroglycerine, without the latter exuding at ordinary temperatures. Although kieselguhr is quite inert, the resulting plastic mass can be detonated with certainty, by the use of the ordinary type of fulminate detonator.

The proportions of nitroglycerine and kieselguhr vary in the many modern dynamites; but the constituents are usually thoroughly kneaded together to a plastic mass, which is pressed into cartridges of parchment paper, of suitable sizes for placing in bore-holes, etc. Dynamite must be kept dry, and not allowed to freeze; water will displace the nitroglycerine, and freezing causes exudation which impairs sensitiveness. To avoid freezing, the nitroglycerine may be mixed, with dinitroglycol, or some organic nitro-compound, such as a liquid nitrotoluene, which will lower the freezing-point. As nitroglycerine contains more than enough oxygen for its own combustion, it is unnecessary to add any further oxidizing agent. Nearly all dynamites contain a small proportion of calcium or magnesium carbonates as a stabilizer.

Some types of dynamite contain an absorbent combustible, such as wood meal or charcoal, in the place of the inert kieselguhr. In these, potassium or sodium nitrate is generally added also, in order to provide enough oxygen completely to oxidize all combustible material.

Other types contain soluble nitrocellulose in the place of wood meal or charcoal. These form a "gelatinized" type of explosive, and are known as "gelatine dynamites"; a typical composition for one of these is given later: it is intermediate in violence between blasting gelatine and gelignite.

Blasting gelatine and gelignite

These are similar types of high explosive, used for blasting. The former is by far the most violent, and can be used against the hardest rocks. It is a balanced explosive, and one of the most violent known. It has a velocity of detonation of 7,700 metres per second. Its high temperature of explosion somewhat limits its use. It is a uniform gelatinous solid, and loses some of its sensitiveness on prolonged storage. It is unaffected by water.

TABLE 20.A.

PERCENTAGE COMPOSITION OF BLASTING GELATINE, GELIGNITE, AND GELATINE DYNAMITE.

	Blasting Gelatine	Gelignite ("60" Gelignite)	Gelatine Dynamite
Nitroglycerine ...	91·5	60·5	74·5
Collodion cotton (soluble nitrocelulose)	8·0	4·5	5·5
Wood meal	—	7·0	4·0
Potassium nitrate ...	—	27·0	15·5
Calcium carbonate ...	0·2	0·2	0·2
Moisture	0·3	0·8	0·3

The calcium carbonate is a stabilizer, which serves to neutralize any small traces of acid set free by decomposition. These explosives should not be stored at a higher temperature than 120° F., as both nitroglycerine and nitrocellulose tend to decompose when stored under such conditions. In all three explosives, part of the nitroglycerine may be replaced by dinitroglycol to prevent freezing.

Ammonal

Composition.

Ammonium nitrate	65
T.N.T.	15
Aluminium powder (heavy)	17
Charcoal	3

Properties and uses.

A fine grey powder which is hygroscopic and very insensitive to shock. Its velocity of detonation is about 3,450 metres per second. It was extensively used for filling bombs and grenades, but is now replaced for bombs by amatol. For grenades, baratol (Chapter XVIII) is becoming the standard filling.

Alumatol

Composition.

Ammonium nitrate	77
T.N.T. (Grade 3)	20
Fine aluminium powder	3

The percentage of aluminium powder varies, but in each case this is designated by a number. The above composition, for example, would be designated " Alumatol 3 ".

Properties and uses.

A silver grey powder, which is hygroscopic, but flows very freely, so that it can be filled through small orifices. It is a substitute for ammonal, and has been used as a bomb and grenade filling, but is obsolete for future filling.

Picramite

Composition.

Ammonium nitrate	72
Ammonium picrate	28

Properties and uses.

A yellow powder, which is hygroscopic. Its explosiveness is deadened by moisture. It cannot be used in the presence of any material containing lead, lest the dangerously sensitive lead picrate should be formed. It has been used for grenades and bombs, into which it was stemmed by hand. It is less violent, but also less sensitive than lyddite, and is considerably cheaper.

Ophorite

Composition.

Potassium perchlorate	60
Magnesium powder	40

Properties and uses.

A fine powder of silver grey appearance, originally proposed as a flashlight mixture. It is dangerously sensitive to both friction and percussion, and needs special care in handling. It is very easily ignited, is not hygroscopic, and has an explosive violence similar to that of gunpowder. Its important characteristic is the great incendiary effect of its explosion; it is therefore used as a mild burster for bombs or shells with fillings that require ignition; *e.g.* smoke, or thermit types of incendiary shells. It was so used as a " burster " for chemical shell during the Great War.

Permite or Palmerite

Composition.

Ammonium perchlorate	82
Zinc dust	10
Mineral jelly	5
Asphaltum varnish	3

Another type contains potassium perchlorate and sulphur, in addition to the above. A mixture of methyl alcohol and benzene is used as a solvent.

Properties and uses.

It is an ammonal type of explosive, with aluminium replaced by zinc. It is, however, sensitive, and its use was thus limited to fillings for bombs and grenades, which are not subjected to severe shock. It is a fine dark brown powder. The addition of mineral jelly and asphaltum varnish reduces its sensitiveness to shock or friction, and confers resistance to the action of water. It is now obsolete.

Blastine

Composition.

Ammonium perchlorate	63
Sodium nitrate	23
Dinitro-toluene	8
Paraffin wax	6

Properties and uses.

A hygroscopic high explosive which has been used for mining operations, and in trench warfare. Its high oxygen content prevents the formation of poisonous gases on detonation. The addition of paraffin wax to this and other mixtures, reduces sensitiveness to shock and friction.

Further compositions are :

Composition	R.D. Composition "B"	R.D. Composition No. 30.
Ammonium perchlorate ...	80	78
Wood meal	5	—
Aluminium powder ...	—	6
Paraffin wax	15	16
Appearance	White, or faint brown granules.	Soft, silver-white granules.

Properties and uses.

Both have been used in mines, being powerful high explosives with a velocity of detonation of about 5,000 metres per second. They are not sensitive to shock ; but are readily ignited by flame, or by frictional blows. When ignited they burn most fiercely, and are very hard to extinguish.

Tonite

Composition.

Guncotton	50
Barium nitrate	50

Charcoal is sometimes added ; and another type contains dinitrobenzene and chalk.

Properties and uses.

The high oxygen content prevents the formation of poisonous gases. Put up in waterproof cartridges, it is used for blasting and similar purposes. It is also used to give the report in service sound rockets, and has been employed in grenades. Unconfined it burns without explosion, and is much safer than guncotton, not being so sensitive to percussion or friction. It should not be stored at a temperature greater than 120° F.

Bellite

A mixture of 83 per cent. of ammonium nitrate, with 17 per cent. of meta-dinitro-benzene, has been used for filling bombs and grenades, and as a mining explosive.

Sonite

A mixture of guncotton and "soluble nitrocellulose" with 1 per cent. of mineral jelly, gelatinized with an acetone-alcohol mixture, has been used for smokeless blank charges.

Sabulite

Composition.

Ammonium nitrate	77·8
Calcium silicide	14·2
T.N.T.	8·0

Properties and uses.

A sage green, dark brown, or black, hygroscopic powder. It is more sensitive than lyddite, and its use was restricted to bomb and grenade fillings, in which capacity it is not likely to be subjected to violent shock. The use of calcium silicide as a combustible ingredient may be noted. Sabulite is obsolete as a Service explosive.

Cilferite

Composition.

Ammonium nitrate	78·5
Ferro-silicon	13·75
Aluminium powder	2·75
Wood meal	5·0

Properties and uses.

A hygroscopic powder that is not damaged by high temperatures of storage. It has been used as a grenade filling. Though not at present in use, it is included as an interesting example of an extra-supply explosive. The inclusion of ferro-silicon (giving the explosive its name) as a combustible material in an explosive, has not been met with previously.

R.D. Composition. No. 202

Composition.

Ammonium perchlorate	77
Charcoal	20
Starch	3

This is a special preparation for the time rings of long-burning fuzes. It will continue to burn even under adverse conditions of rapid spin of shell, and low atmospheric pressure. The products of combustion are entirely gaseous, and there is no formation of slag. The composition is slightly more sensitive to friction than ordinary fuze powder, and its rate of burning is more susceptible to changes of temperature. (*See* Chapter XXII.)

G.—INITIATORS AND GUNPOWDER.

CHAPTER XXI

MERCURIC FULMINATE, CAP COMPOSITIONS, LEAD AZIDE, LEAD STYPHNATE

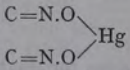
Mercuric Fulminate. Hg. $(O.N.C.)_2$

Introduction.

Mercuric fulminate was discovered by Howard in 1799, and is the mercuric salt of fulminic acid. Various structural formulæ have been assigned to it, but the one which now receives most support is that which was put forward by Nef. Nef considers, on the grounds of experimental evidence, that mercuric fulminate is the mercury salt of the oxime of carbon monoxide (the condensation product of carbon monoxide and hydroxylamine, NH_2OH :

$$CO+NH_2OH \rightarrow \underset{\substack{\text{Oxime of}\\ \text{carbon monoxide.}}}{C:N.OH} + H_2O$$

On this reasoning, mercury fulminate is given the structural formula :



Mercuric fulminate is an endothermic compound, much energy having been absorbed in its formation. It is very unstable, being probably in a state of molecular strain. If subjected to impact, friction, or sudden heating by contact with a flame or a hot wire, it will, if suitably confined, detonate violently :

$$Hg(ONC)_2 \rightarrow Hg+2CO+N_2+122K$$

This breaking up is accompanied by a great evolution of heat. This is due in part to the heat of decomposition of the fulminate, and in part to the exothermic oxidation of the carbon to carbon monoxide.

The degree of violence of the explosion much depends on the state of confinement ; a very small quantity of the fulminate if ignited in the open, may burn without much explosive effect.

Manufacture.

On account of its extreme sensitiveness, mercuric fulminate is manufactured, as far as government factories are concerned, in small quantities at a time by what amounts to a laboratory process, entailing the use of no special plant.

One part by weight of pure mercury is dissolved in 11 parts of nitric acid, sp. gr. 1·36. This forms an acid solution of mercuric nitrate, and copious brown fumes of nitrogen peroxide are given off, and much heat evolved. The solution is allowed to cool, and then poured into a large flask containing 10 parts of 90 per cent. ethyl alcohol at about 20° C. There is a brisk reaction and an evolution of white fumes. These later become brown, then lose their colour, becoming white again. The temperature rises to over 80° C. During the reaction very small crystals of mercuric fulminate begin to separate out. Quantities of about ½ kilogram of mercury are dealt with at a time, and the reaction with the alcohol occupies about half an hour. The flask is allowed to stand and cool, and the liquid is then poured off from the heavy fulminate which settles to the bottom. The latter is agitated with several washings of fresh water in the flask, all traces of acid being thus removed. The fulminate is finally separated on a muslin filter. It is stored in the wet condition in which it is comparatively safe, and most carefully dried at a low temperature as required for use.

Properties and uses.

Made as above, the product resembles grey or brownish sand. It is sometimes bleached white in manufacture by the addition of a small quantity of a copper salt to the solution of mercury in nitric acid ; but this makes little difference to the final product beyond the change of colour.

It is a substance of high density, 4·45 ; but when loose, its apparent density is only 1·7. This is increased to about 3·5 to 4 by compression, in the manufacture of detonators, etc. Compression decreases its sensitiveness to flash, and if carried to an excessive extent markedly reduces the violence of the detonation of the fulminate ; in this condition it is said to be " dead pressed ".

It is very sparingly soluble in water either hot or cold, and is not hygroscopic, but when moist is readily decomposed by many metals, freeing metallic mercury and forming fulminates of other metals, which are often more unstable than the mercuric salt. For this reason it is usually protected in detonators, etc., by a film of varnish which prevents the access of moisture. It is soluble in alkaline iodides and cyanides, and in sodium thiosulphate. It is decomposed by the latter, and this reaction is used for the analysis of fulminates. It is extremely poisonous. It ignites, with detonation, at 185° C.

Mercuric fulminate is more sensitive to shock or friction than most high explosives, and is very violent when detonated. Although its velocity of detonation is low (of the order of 3,000 metres per second), a comparatively small impulse suffices to bring it to its full rate of detonation very quickly.

It is used in detonators, either alone, or mixed with from 10 per cent. to 20 per cent. of potassium chlorate; it is also the most active constituent of many cap compositions. Its extreme sensitiveness limits the quantity that can be safely used in a detonator that is to be fired from a gun, and it is for this reason that exploder systems containing intermediaries are necessary in modern shells filled with comparatively insensitive high explosives.

Detonators are made in various forms, and may be initiated by means of a blow, or a high temperature flame produced by suitable means.

Cap Compositions

These are sensitive mixtures which are usually enclosed in some form of percussion cap. They are exploded by piercing with a needle, or by a blow from a striker. Similar mixtures are used in friction tubes, and in this case rubbing on a rough surface is the initiating agency. By the use of cap compositions, an inflammation, or an explosion, as distinct from a detonation, is initiated.

The main sensitive constituent is mercuric fulminate, but as little flame is produced when this is used alone, such as there is being of very short duration, the fulminate is usually mixed with both potassium chlorate and antimony sulphide. The former increases the heat of explosion, and the latter prolongs the flame effect. To diminish the violence, sulphur and gunpowder are also included in certain cap compositions; powdered glass is sometimes used to increase the sensitiveness to friction, and a small proportion of gum or gelatine may also be added to bind the materials together. In certain compositions such as those used in friction tubes, the dangerously sensitive mercuric fulminate may be dispensed with altogether.

The following are some typical compositions, the proportionate quantities being given in approximate percentages for purposes of comparison.

TABLE 21A.

	S.A. Percussion caps		Cap in German T. & P. Fuze	Friction tube British	Detonating Composition "A" Mixture "6.6.4" British
	British	Austrian			
Mercuric fulminate ...	19·0	14	16·5	Nil	37·5
Potassium chlorate ...	33·0	42	50·0	44·6	37·5
Antimony sulphide ...	43·0	34	33·5	44·6	25·0
Gunpowder	2·5	Nil	Nil	3·6	Nil
Sulphur	2·5	Nil	Nil	3·6	Nil
Powdered glass ...	Nil	10	Nil	3·6	Nil

In the above German and Austrian compositions, a very small proportion of gelatine is also added to bind the materials together. The potassium chloride formed as a product of explosion of S.A. cap compositions containing potassium chlorate has a tendency to corrode rifle barrels, and many attempts have been made to produce a cap composition without this ingredient.

The nature of these mixtures precludes incorporation by any milling or similar process. The constituents are ground separately, and passed through sieves to eliminate any comparatively large particles of extraneous gritty matter. The materials are mixed dry, by gentle agitation in a conical fabric bag known as a " jelly-bag," in which are a number of loose rubber balls. For the safety of the worker the bag is operated from behind an iron screen.

Such sensitive mixtures are usually transported and stored in small boxes of papier mâché or other soft material.

The mixtures are filled into metal caps and brought to a sufficiently dense state within them by a certain amount of compression ; the surface of the material is then protected by a coating of waterproof varnish and sometimes also by metal foil.

Lead Azide PbN_6

Azides are salts of hydrazoic acid HN_3. The latter can be isolated in a pure state. It is soluble in water, and in solution dissolves metals such as iron, zinc and copper forming metallic azides and liberating hydrogen. Both the acid and its salts are, in general, extremely poisonous. Most metallic azides are very sensitive and powerful explosives. Those of mercury, silver and lead can be employed as initiators in a similar manner to mercuric fulminate.

Preparation.

Lead azide is obtained as a crystalline deposit on adding a solution of sodium azide to a solution of a soluble salt of lead, such as the acetate.

Sodium azide is not sensitive to shock and may be prepared from hydrazine (N_2H_4) in alcoholic solution, by treatment with ethyl nitrite and caustic soda :

$$N_2H_4+C_2H_5NO_2+NaOH \longrightarrow NaN_3+C_2H_5OH+2H_2O$$

or by heating sodamide in a current of nitrous oxide :

$$2NaNH_2+N_2O=NaN_3+NaOH+NH_3$$

The subsequent stages of the process are of a dangerous nature, since lead azide is extremely sensitive. The operations are carried out under rigid precautions, and only small quantities of the order of 300 grams are made at a time.

Equal volumes of equivalent solutions of sodium azide and lead acetate are run into water in a highly glazed pan, and the mixed solutions stirred by a rotating paddle.

$$2NaN_3+Pb(CH_3COO)_2 \longrightarrow PbN_6+2CH_3COONa$$

For safety in subsequent stages of manufacture, and in later handling, great care has to be paid to the details of the process in order to obtain the lead azide in a suitable physical form. Unlike mercuric fulminate, lead azide is sensitive whether it is wet or dry, and is not rendered safe by immersion in water ; prolonged contact with water is conducive to the formation of large crystals which are extremely sensitive, and which may detonate spontaneously.

The lead azide is washed several times in the mixing pan, the wash waters being decanted off by special gear. The azide is then flushed on to a filter and is there washed again. It is next transferred to drying pans where the water is driven off at a temperature of 140° F.

The azide is finally sieved through silk, with mechanical agitation. All mechanical operations are controlled from outside the building in which they take place, and all moving parts where shock or friction might occur are protected by felt pads.

Properties and uses.

As prepared above, lead azide is in the form of very small crystals like fine white sand. It tends to become greyish brown, due to decomposition, on exposure to light. It is practically insoluble in cold, and only slightly soluble in hot water. Solution in nitric acid in the presence of a nitrite is used as a means of destruction ; this avoids the production of the poisonous hydrazoic acid which occurs if nitric acid is used alone.

Lead azide is decomposed on prolonged heating with water.

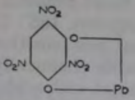
Its true density is about 4·8, but the apparent density of the loose powder is only about 1·2. Its ignition point is high (320°–390° C.).

Lead azide is slightly less sensitive to friction than mercuric fulminate, and much less sensitive to blows and to pricking by a needle. It attains its maximum rate of detonation very rapidly, and compared with mercuric fulminate, a much smaller quantity is required to initiate detonation in other high explosives.

It does not exhibit the tendency, shown by mercuric fulminate, of becoming insensitive to flash when highly compressed (" dead-pressed "). But its chief advantage over mercuric fulminate is that it does not deteriorate rapidly with hot dry storage. Dry mercuric fulminate is seriously deteriorated after about three or four months at 120° F. whereas lead azide is not appreciably affected after a year under these conditions.

Lead azide is used both in percussion detonators and in detonators which are ignited by a flash. On account of its comparatively insensitive character, it is generally used in conjunction with a layer of a suitable priming composition.

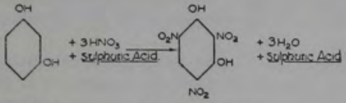
Lead Styphnate



Lead styphnate is the lead salt of trinitro-resorcinol (styphnic acid), which is prepared by the nitration of resorcinol (meta-dihydroxy-benzene).

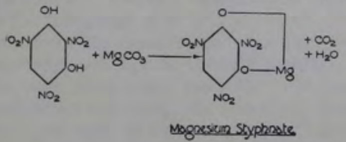
Preparation.

(i) Styphnic acid is made by nitrating resorcinol under the same conditions as are used for making picric acid from phenol (Chapter XVII).

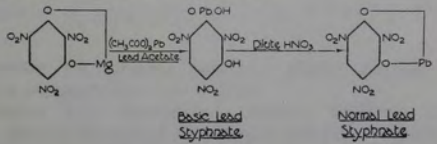


Resorcinol. Styphnic Acid.

(ii) Magnesium styphnate is prepared in solution by dissolving styphnic acid and magnesium carbonate in hot water :



(iii) The solution of magnesium styphnate, at 70° C., is added to a well-stirred solution of lead acetate, also at 70° C. A thick precipitate of basic lead styphnate is formed. Stirring is continued for 15 minutes, and then dilute nitric acid is added to convert the basic salt to normal lead styphnate.



The temperature is dropped from 70° to 30° C., stirring is stopped, the lead styphnate is allowed to settle, is washed three times with water by decantation, filtered off, washed with alcohol, and finally dried in air. It is then sieved through silk. Operations (ii) and (iii) are performed in glazed porcelain vessels.

Properties and uses.

Lead styphnate forms short rhombic crystals. It is poisonous. It ignites at 255° C. (as against 185° C. for mercuric fulminate). Lead styphnate is somewhat less sensitive to friction than mercuric fulminate, and is quite stable chemically. It must not, however, be allowed to come into contact with acids, oxidizing agents, sulphur, sulphides or grit.

Lead styphnate is used as a constituent of compositions used for the priming layer of lead azide detonator ignited by a flash.

CHAPTER XXII

GUNPOWDER, SLOWMATCH, QUICKMATCH, AND FUZE COMPOSITION

Gunpowder

Introduction.

Gunpowder is the oldest explosive in existence, and its origin is unknown. It remains an important explosive, but is now little used as a propellant. A brief résumé of its history is given in Chapter III.

Gunpowder consists of charcoal, saltpetre and sulphur, in various proportions. It is a mechanical mixture of solid particles, and its structure is therefore quite unlike that of the cordite type of propellant in which the mixture is of the more intimate colloidal nature.

The ingredients in themselves are not explosive. Charcoal is the combustible element present ; saltpetre is the oxygen carrier ; sulphur lowers the temperature of ignition.

It is obvious from its constitution that the products of combustion of gunpowder will not be entirely gaseous. This is so far from being the case, that more than half (56 per cent.) of the products of combustion are solids, the remainder being gaseous and including about 1 per cent. of water vapour. These solid products were the source of two of the many disadvantages of gunpowder as a propellant, since they caused rapid fouling of the weapons, and produced large clouds of dense white smoke on discharge.

Manufacture of Gunpowder

Five grades of gunpowder are being retained in the Service. These are :

Gunpowder P3. Pebble powder ; passes through a ¾-inch sieve and is retained on a ⅜-inch sieve.

Gunpowder G7. Granulated powder, formerly known as R.L.G.2 ; passes through a ¼-inch, and not less than 95 per cent. is retained on a No. 8 B.S. sieve.

Gunpowder G12. Granulated powder, formerly known as gunpowder R.F.G.2 or gunpowder F.G. ; passes through a No. 8 B.S. sieve and not less than 95 per cent. is retained on a No. 16 B.S. sieve.

Gunpowder G20. Granulated powder, formerly known as gunpowder S.M.I. or gunpowder R.P.P.; passes through a No. 16 B.S. sieve and not less than 95 per cent. is retained on a No. 25 B.S.

Page 162. *After* line 4 *insert* :—

X — Gunpowder G.40. Introduced in 1939. Passes a No. 25 B.S. sieve and not less than 95 per cent. is retained on a No. 52 B.S. sieve. am 1

The manufacture may be divided into various operations, *e.g.* Grinding, Incorporating, etc.

1. *Grinding.* The three ingredients are ground separately, foreign matter being removed by sieving.

2. *Weighing.* The constituents are weighed separately in the proper proportions, which are: saltpetre, 75 per cent.; charcoal, 15 per cent.; and sulphur, 10 per cent. In weighing out, the proportion of saltpetre is often increased slightly to allow for the small amount of moisture that is usually contained in it.

3. *Preliminary mixing.* The ingredients are placed in a cylindrical drum on the axle of which are mounted a number of radial arms. The drum and the arms rotate in opposite directions at different speeds, and mixing is completed in about five minutes. This operation is followed by sifting through a fine-mesh wire gauze. This sifting is important, since it frees the mixture from large hard particles which, in the subsequent operations, might give rise to an explosion.

4. *Incorporating or milling.* Iron edge-runner mills similar to those used in mixing mortar, are used. In the latest types (Fig. 22.1) the runners are supported in such a manner that there is a small clearance between them and the iron bed-plate on which the powder is placed. The runners are pivoted in such a way as to allow of independent movement in a vertical direction. In the earlier types of mill, the runners might be either of iron or stone, and were allowed to rest freely on the bed-plate.

Two wooden ploughs rotate with the edge-runners, stirring up the charge and preventing it from accumulating at the centre and curb of the bed-plate. According to the size of the mill, the normal charge varies from 80 to 140 lb. Any decrease in the standard amount is avoided, as likely to lead to an explosion.

The mills are isolated by strong masonry walls, and the danger of explosion during milling is minimized by keeping the charge damp. Automatic drowning arrangements are provided for each mill.

The incorporation is an important operation in the manufacture, and to obtain uniform and quick-burning powders long times of incorporation (4 to 6 hours) are necessary. During the Great War "short-milled" powders were introduced, in which the time of incorporation was reduced from about six hours to two. These powders are now obsolete, but they may be reintroduced in case of emergency.

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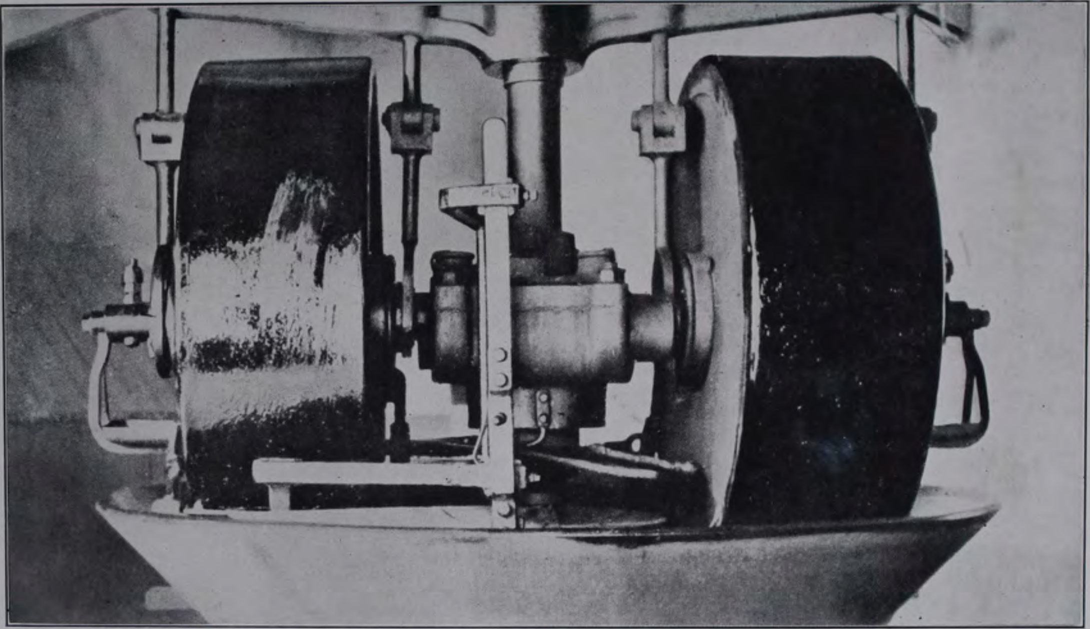

Fig. 22.1.—Gunpowder Incorporator Mill.

Gunpowder G20. Granulated powder, formerly known as gunpowder S.M.I. or gunpowder R.P.P.; passes through a No. 16 B.S. sieve and not less than 95 per cent. is retained on a No. 25 B.S. sieve.

Mealed powder. Passes a No. 150 B.S. sieve and not more than 25 per cent. is retained on a No. 240 B.S. sieve.

The manufacture may be divided into various operations, *e.g.* Grinding, Incorporating, etc.

1. *Grinding.* The three ingredients are ground separately, foreign matter being removed by sieving.

2. *Weighing.* The constituents are weighed separately in the proper proportions, which are: saltpetre, 75 per cent.; charcoal, 15 per cent.; and sulphur, 10 per cent. In weighing out, the proportion of saltpetre is often increased slightly to allow for the small amount of moisture that is usually contained in it.

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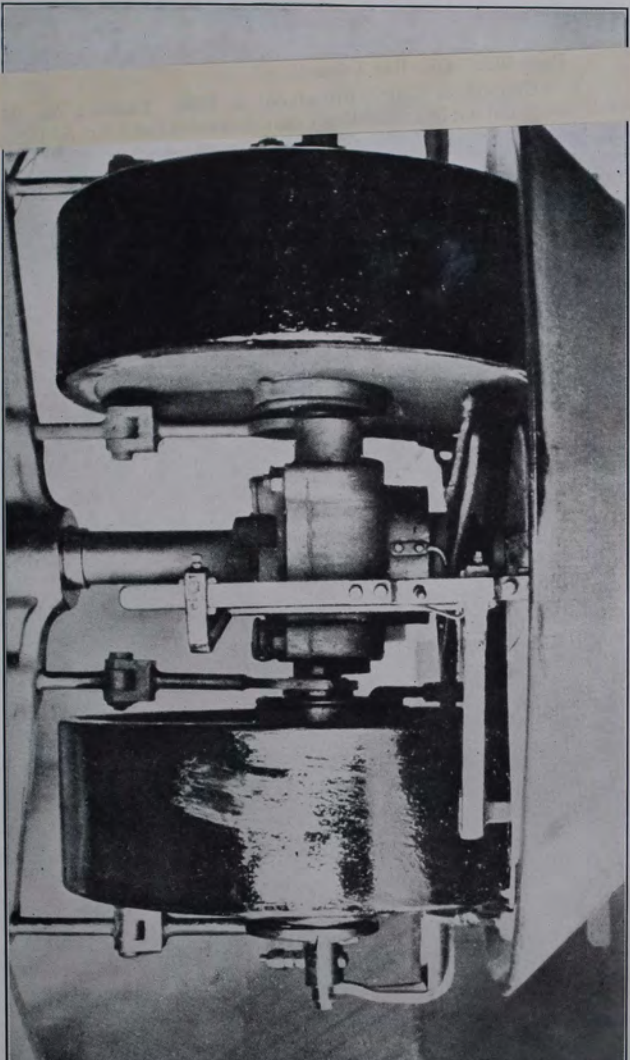

FIG. 22.1.—Gunpowder Incorporator Mill.

The product of milling is known as "mill-cake". The mill-cake contains hard pieces formed under the weight of the runners, and as these pieces may adhere to the bed-plate, great care has to be exercised in emptying the mill. Only wooden tools are used. In the older mills, a small quantity of powder is usually left to support the runners, and if it is necessary to empty the mill entirely, the runners are moved on to leathers. This avoids the risk of ignition being caused by a small amount of powder being nipped between the runners and the iron bed-plate.

5. *Breaking down.* The mill-cake is broken up either by hand, or by passing it between gunmetal rollers.

6. *Pressing.* The mixture is compressed into a hard dense mass in a hydraulic press. A press charge is built up of a number of layers of powder on copper sheets. The layers are "struck off" level in a wooden frame which is then removed, and the powder is thus not confined during the pressing operation, owing to the danger of friction against the sides. The copper plates may be as large as 30 inches square, and a number of layers of powder, each about 1 inch deep are built up so that the quantity pressed in one operation may be as much as 1,000 lb.

Pressure is applied until a predetermined contraction in height is obtained, the load being of the order of 600 to 800 lb. per square inch, but varying according to the nature of the materials employed, and the density required. The product is known as "press-cake".

Pressing is a dangerous part of the manufacture of gunpowder. Each press is carefully isolated, and no one is allowed in the building during pressing. The necessary controls for the press, and means for observation, are contained in a building separated from the press-house by a mound.

7. *Granulating (Corning).* The press-cake is passed through a series of rollers which break it up. The first rollers are usually toothed, then follow serrated rollers, while the final set are usually smooth. Of each pair of rollers, one is driven on fixed bearings, while the other is mounted on sliding bearings held either by springs or by levers with counter-balancing weights. This arrangement allows the rollers to move apart, and should any large and hard object find its way into the powder, it is enabled to pass through the rollers without producing an excessive amount of friction or heat. Between each set of rollers is an automatic sieve, which passes the powder on to the next set of rollers, or returns it to the previous set for regrinding. Any dust or fine powder is collected, and, after re-incorporation and pressing, is once more granulated. Isolation of the units is necessary, as the operation is dangerous.

Powders, which are particularly liable to be dusty, such as those made from Dogwood charcoal, are dusted in a special machine arranged for that purpose.

8. *Glazing*. Slow-burning powders are glazed by rotation in a wooden drum with a little graphite. This process rounds the grains, increases the density of the powder and renders the surface less porous, so impeding the progress of the flame from one grain to another.

Other powders are glazed for a longer period in the same way, but without the addition of graphite.

9. *Drying*. Gunpowder is dried by steam heat from one to four hours at 40° C. The amount of moisture normally present is about 1 per cent., a quantity which is in equilibrium with the average atmospheric conditions.

10. *Finishing and blending*. The last traces of dust are removed by rotating the powder in a wooden cylinder lined with canvas, for two hours.

Blending is accomplished by collecting the powder from several batches in a large hopper, which is furnished with four outlets. The contents of the hopper are thus divided into four equal portions. By returning these to the hopper and repeating the operation, blending is rapidly and easily completed.

Properties of Gunpowder

Gunpowder burns vigorously with the evolution of large quantities of white smoke. It cannot be detonated, as it is a mechanical mixture and the constituents are not, in themselves, explosive.

It is quite stable in storage. Moisture affects gunpowder, rendering it more difficult to ignite, and excessive wetting may also cause the solution and segregation of some of the saltpetre. The effect of a damp atmosphere on the saltpetre is not so great if the latter is absolutely pure.

Gunpowder ignites at about 300° C. Under the falling weight test gunpowder has a figure of insensitiveness of 90 (picric acid =100). The rate of progration of explosion in gunpowder can be made slower in many ways, viz. by decreasing the percentage of saltpetre, by compressing to a high density, or by making a coarser grained powder.

The ordinary black powders are porous, and hence the flame penetrates to the interior, resulting in a very rapid burning of the whole mass. The brown or " cocoa " powders were less porous, and therefore they burnt more evenly from the surface.

When exploded, as has already been mentioned, gunpowder produces solid and gaseous material. The solid products of combustion are chiefly potassium carbonate, potassium sulphate and potassium sulphide, with a small quantity of potassium thiocyanate, and traces of free sulphur ; the gases are chiefly carbon dioxide and nitrogen, and a little water vapour.

Good gunpowder is free from dust, well glazed, hard, crisp, and of a good colour. These qualities can be estimated by visual examination. In addition tests are carried out to ascertain :

(*a*) Thoroughness of incorporation.
(*b*) Size, shape and uniformity of the grains.
(*c*) Density.
(*d*) Moisture content.
(*e*) Capacity for absorbing moisture. (hygroscopicity tests) am1
(*f*) Proportions and purity of the ingredients.

Gunpowder is used in the Service for the following purposes :

(i) Blank charges.
(ii) Charges for firing paper shot.
(iii) Igniters of most cordite cartridges.
(iv) Fuzes and tubes.
(v) Combustible composition, *e.g.* quickmatch, priming and cap compositions.
(vi) Bursting charges of some shell, *e.g.* shrapnel, and base ejection shell.
(vii) Many pyrotechnic stores.

It is much used commercially for demolition and blasting purposes.

Sulphurless Gunpowder

Sulphurless gunpowder consists of a mixture of 70·5 parts of saltpetre and 29·5 parts of charcoal. It is manufactured in the same way as gunpowder. It was originally introduced for the igniters of cordite cartridges because the sulphur in ordinary gunpowder had a bad effect on Cordite Mark I.

Its use in igniters is now obsolete, but it is used to a considerable extent in pyrotechnic stores, since many pyrotechnic compositions form sensitive or unstable mixtures with sulphur.

Slowmatch

Slowmatch consists of slightly twisted hemp boiled in a solution of wood ashes (potassium carbonate) and water, or in a solution of saltpetre (potassium nitrate) in water (8 oz. in 1 gallon).

It burns at the rate of 1 yard in 8 hours, and is used for lighting portfires, etc.

Quickmatch

This consists of cotton wick impregnated and coated with a paste of sulphurless mealed powder and gum. When nearly dry, it is dusted with mealed sulphurless gunpowder.

Quickmatch burns at the rate of one yard in 30 seconds, but when enclosed it burns much more rapidly. It is largely used for priming rockets, and in the construction of pyrotechnic stores.

Instantaneous Fuze

Fuze Instantaneous Mark III/L/, consists of two or more strands of quickmatch enclosed in a tube of waterproof tape, which is surrounded by a layer of twisted cotton. The final covering is a gutta-percha tube, braided with cotton yarn on the exterior. This is varnished orange or yellow. The colour, and the cotton braiding serve to distinguish it, both to the eye and to the touch, from safety fuze.

Instantaneous fuze burns at the rate of 30 yards a second.

Safety Fuze (Bickford Fuze)

Safety fuze consists of a train of fine-grained gunpowder enclosed in a casing of jute yarn. The fuze is treated with a waterproofing composition, and finished with a further layer of threads or waterproof tape.

There are several types of safety fuze in the Service, differing in rate of burning and in dimensions. They are designated by numbers, and can be distinguished by the colour of the external coating. No. 9 fuze, for instance, is black and burns at the rate of 1 yard in 75 to 105 seconds.

Time-Fuze Compositions

Ordinary time-fuze powders, such as 20-second and 30-second compositions for use in the time rings of fuzes, have the approximate constitution given below :

Potassium nitrate	74–76 parts
Sulphur	8–10½ ,,
Charcoal	18–13½ ,,

For special purposes, Composition S.R. 227 was developed, the ingredients being in the following proportions :

Potassium nitrate	72 parts
Sulphur	7 ,,
Charcoal	21 ,,

The compositions are made in the same manner as gunpowder, but great care is taken in the selection, manufacture and blending of the constituents. The powders are made in lots and carefully blended, so as to obtain the specified time of burning.

The time rings are filled by pressing in the composition. Careful regulation of the pressure of filling is necessary. The time of burning of a fuze composition can be varied, within limits, by three means ; (*a*) Control of the time of incorporation ; (*b*) treatment and blending of the charcoal ; (*c*) final blending of different powders.

(*a*) *Control of the time of incorporation.* The rate of burning increases with the time of milling up to a maximum time of milling of 12 hours. Milling for any longer period has no effect on the rate of burning, but may be slightly beneficial in other directions.

(*b*) *Treatment and blending of the charcoal.* Charcoal from different woods may be blended to give definite times of burning. For example, the charcoal from lignum vitæ, a hard wood, can be used as a slowing agent.

Variations in the time of charring produce charcoals which vary in their effects on the time of burning.

(*c*) *Blending of different powders.* Powders which burn at different rates may be blended to produce a powder with the desired mean time of burning.

For anti-aircraft purposes, fuzes which are quite successful for fire at low elevations have proved to be entirely unsuitable. Investigations of the factors influencing the behaviour of time-fuze compositions under varying conditions were carried out during the Great War in the Engineering Laboratory of the University of London. An exhaustive description of these tests and the results obtained will be found in the " Text Book of Anti-Aircraft Gunnery," Volume I.

The trials comprised the burning of various types of fuzes and fuze compositions under varying conditions of pressure, temperature and rate of spin.

From the results obtained, it is evident that the factors affecting the successful operation of a time fuze, are (*a*) External and (*b*) Internal.

(*a*) External factors comprise the following :

> Rotational speed, pressure on the burning surface, temperature of composition in the rings, humidity of the air.

(*b*) Internal factors are those inherent in the fuze composition itself, *e.g.* formation and nature of slag.

The factors under heading (*a*) were thoroughly investigated in the trials referred to above, and the reader is referred to the book already mentioned, and to the Text Book of Ammunition (1936), for further details. In general, these factors can be considered as outside the control of either the producer or the gunner. Their effect, however, can be measured and allowed for in the fuze setting.

As regards (*b*) more may be said here. The successful performance of the fuze is dependent on the quality and on the nature of the composition used, and on the details of construction and method of filling the fuze rings. The non-gaseous products of the fuze composition at the temperature of combustion are plastic and can, under the action of the centrifugal force, interfere with the venting of the gases, giving rise to fluctuating pressures and irregularity of burning. The fluidity of the slag is enhanced by increase in the proportion of sulphur, and for this reason fuze compositions should not contain more than 10 per cent. The ability of gunpowder fuze composition to burn in the low pressures attained in high-angle fire is determined by the nature of the charcoal employed. The best wood for the

TABLE 22A.

GUNPOWDERS

Type	Number	COMPOSITION			SIZE (B.S. SIEVES)		NOTES
		Per cent. Pot. nitrate	Per cent. Charcoal	Per cent. Sulphur	Passed	Retained	Correspond to :
Cut or " Pebble "	P.3	—	—	—	$\frac{3}{4}''$	$\frac{3}{8}''$	P., Shell D.P.
Granulated	G.7	—	—	—	$\frac{1}{4}''$	No. 8 (not less than 95 per cent.)	R.L.G.
do.	G.12	75	15	10	No. 8	No 16 (not less than 95 per cent.)	R.F.G., L.G., etc.
do.	G.20	—	—	—	No. 16	No. 25 (not less than 95 per cent.)	S.M.I., R.P.
Mealed	Mealed	—	—	—	150	240 (not greater than 25 per cent.)	—
Special for Time Rings of Fuses.	S.R.227	72	21	7	—	—	—
Sulphurless Mealed	—	70·5	29·5	—	—	—	For Igniter pellets, quickmatch, etc.
do	G40	-	-	-	No 25	No 52 (not less than 95%)	

Current

am 1

NOTE. Before the introduction of Cordite, Gunpowder was produced in several moulded forms such as cylinder, spheres, and prisms.

purpose is dogwood, and the degree of carbonization is controlled to give a product containing about 65 per cent. of carbon.

Attempts have been made to produce slagless compositions; one of the most successful being Research Department Composition No. 202 (*see* Chapter XX).

Ammonium perchlorate	77 parts
Charcoal	20 ,,
Starch	3 ,,

This composition has the additional advantage of giving very long times of burning.

Finality in the design of time fuzes is far from being reached, and the subject offers a wide field for further investigation.

H.—MISCELLANEOUS COMPOSITIONS

CHAPTER XXIII

ILLUMINATING, SIGNAL, SMOKE AND INCENDIARY COMPOSITIONS.

The compositions mentioned in the third main category of the service classification of Explosives in Chapter II remain to be considered. This chapter deals with Pyrotechnics (Greek *pyros* =fire, *teknikos*=art).

For some amplification of the matter contained in this chapter, the reader is referred to " The Armament Training Manual for the Royal Air Force. Part II, Chapter V (Pyrotechnic Compositions)—Air Ministry, 1927, official use only.

Illuminating and Signal Compositions.

Introduction.

Illuminating compositions are required to give an intense light, and are used for disclosing the position of hostile troops at night and for other purposes. The colour of the light is not materially important, but the intensity should be as high as possible. Light of the brightness required is obtained by the combustion of compositions containing aluminium or magnesium powders. Oxidizing agents, such as nitrates or perchlorates, are incorporated to supply the necessary oxygen for the combustion of the metals.

Signal compositions are of two kinds :

(*a*) *For night use.* Since sources of light of small intensity are visible at night from long distances, the chief requirement of signal compositions is distinctiveness.

Certain salts impart an intense and characteristic colour to a flame with which they are brought in contact. Thus, sodium salts give a brilliant golden-yellow colour to a flame. An example of an everyday application of this phenomenon is to be found in the sodium-vapour lamps which are now used to light some main roads by night. This golden-yellow colour is characteristic of all incandescent sodium salts, and is given even by minute amounts of such salts.

Other metals whose salts impart a characteristic colour to a flame are :

Metal	*Flame colour*
Barium	Green
Calcium	Orange red
Copper (as basic copper carbonate)	Blue
Potassium	Violet
Strontium	Red

Salts of these metals can, therefore, be used to impart the requisite colour to signal compositions for night use. It may here be noted that compositions, other than those which are required to give a yellow light on burning, must be free from traces of sodium salts, for the very intense yellow sodium light is apt to mask the feebler colours which are given by the other metallic salts.

(*b*) *Signal compositions for day use.* The above signal compositions are only visible at short distances in bright sunlight, and coloured smoke signals are often used in their place. The coloured smokes are obtained by the thermal atomization of a dyestuff, the necessary heat being derived from the combustion of a suitable composition, with which the dyestuff is intimately mixed. The heat produced by the composition must not be too great and must be sufficient to volatilize the dyestuff but not to burn it up.

General remarks on the method of preparing and filling.

The rate of burning of a pyrotechnic composition varies according to its state of aggregation. If the composition is in the form of a powder, it will burn rapidly on ignition, and may even explode. When compressed to uniform density in a container, the composition behaves like a cordite, and burns slowly and regularly, layer by layer. Such a method of filling will give a constant rate of burning, provided that the escape of the gaseous products of combustion is not impeded by the container or by slag.

If the free escape of such gases be prevented in any way, the gaseous pressure on the burning surface will rise, and the composition will burn irregularly and may even explode.

The regulation of the rate of burning is the most important characteristic which has to be considered when deciding on the proportions of the ingredients and the method of filling of a pyrotechnic substance. The variables which influence rate of burning will now, therefore, be considered :

(*a*) With many compositions, the production of the best effect necessitates that the specified proportions of each ingredient be strictly adhered to.

(*b*) Most ingredients contain traces of impurities, and it is necessary to lay down certain standards of purity for these ingredients, since impurities sometimes exert a very deleterious effect on rates of burning.

(*c*) The rate of burning of a composition depends on the pressure by which the composition is consolidated. Up to pressures of 6 tons per square inch the rate of burning decreases with the pressure used in consolidating the composition. Increase of this pressure over 6 tons per square inch has little further effect on the rate of burning.

(*d*) The degree of subdivision of the various ingredients, especially metallic ingredients, is important. The larger the particles, the slower will be their rate of burning, since the burning of a pyrotechnic composition is essentially a surface action.

(*e*) The apparent density of the ingredients has also to be considered, for the apparent density is to some extent controlled by the shape and dimensions of the individual particles.

Illuminating Compositions

Ingredients.

The oxidizing agents used in admixture with magnesium or aluminium powders to form illuminating compositions are usually nitrates. Perchlorates are sometimes used, but compositions containing chlorates are too sensitive for use. Other ingredients employed to alter the rate of burning and/or the character of the flame are organic materials such as lactose, wood-meal and acaroid resin.

Stability

The most likely cause of deterioration of an illuminating composition is the reaction of the powdered metals with moisture. Powdered metals have a large surface and may react vigorously with water or damp air, liberating hydrogen (which may inflame) and forming the oxide or hydroxide of the metal. For example, zinc powder may ignite in contact with water.

Powdered magnesium and aluminium also react with water. The ingredients which are mixed with these metallic powders, to form illuminating compositions, usually, though not always, increase the rate of corrosion. The reaction with water of magnesium and aluminium can usually be prevented by coating the particles of the powder with oil or wax, but this treatment does not prevent vigorous reaction with moisture taking place if a salt of a heavy metal, such as copper sulphate, is also used as an ingredient of the composition.

Candle power.

The candle power (c.p.) of an illuminating composition is given by the formula:

$$\text{c.p.} = \frac{\text{E. W.}}{\text{T}}$$

where W is the weight, in grams, of the composition which burns in T seconds, and E is a constant, called the Efficiency of the composition, which is the amount of light produced by one gram of the burning composition in one second. An average value of E for illuminating compositions is 10,000.

Compositions.

The following compositions have been recommended for use in Parachute Star Shell.

" A " composition (greenish white).

Magnesium powder	35 parts
Barium nitrate	59 parts
Paraffin wax	6 parts

The greenish tinge and the dazzling flame produced are due to the magnesium and the barium salt.

" B " composition (white).

Magnesium powder	27 parts
Aluminium powder	9
Barium nitrate	58
Paraffin wax	6
	100

Here, the intense white light from the burning aluminium masks the comparatively feeble green light from the barium salt, and the general light effect is white.

Signal Compositions

Ingredients.

Compositions for night use contain three essential ingredients. An oxidizing agent, which may be a nitrate, perchlorate or a chlorate ; a fuel which is usually an organic substance such as shellac, acaroid resin or lactose ; and a compound containing a metal which will impart the desired colour to the flame.

A composition containing aluminium is often used for the white signal.

The following are typical signal compositions for night use :

Star compositions for Signal Cartridges

White.		*Red.*	
Barium Nitrate	64 parts	*Strontium Carbonate	6 parts
Aluminium Powder	20	Potassium Chlorate	16
Sulphur	16	Calomel	2
		Charcoal	1 to 3
	100	Shellac	3

Yellow		*Green*	
*Sodium Oxalate ...	6 parts	*Barium Chlorate ...	24 parts
Potassium Chlorate...	20	Lactose	8
Shellac	5	Shellac	1
	31		33

* Imparts characteristic colour.

Star compositions for Rockets

Rockets are used for signalling and other purposes. They may discharge illuminating or coloured stars, or may contain a small charge of a high explosive, which is fired by a detonator, to give a loud report. The following is a composition for a blue rocket star :

Blue Star

Potassium Chlorate	50 parts
Basic Copper Carbonate (to give the blue colour to the star)	8
Calomel	32
Shellac	10
	100

Rockets themselves are filled with a composition resembling gunpowder, the composition being varied to suit the speed of burning required.

A typical example is as follows :

Rocket Composition

Saltpetre	85 per cent.
Sulphur	1
Charcoal	14

Rockets are generally ignited by means of a port-fire, which is a slow-burning mixture of saltpetre, sulphur and mealed gunpowder.

(*b*) *Signal compositions for day use.*

Examples of coloured smoke compositions are shown below :

Purple signal smoke for day use		*Yellow smoke*	
Lactose	2	Potassium Nitrate	33
Potassium Chlorate ...	3	Orpiment	38
Gallocyanine (Purple dye)	5	Sulphur	29
	10		100

Gallocyanine is a dyestuff which volatilizes to produce a purple smoke, and orpiment is an arsenic sulphide which volatilizes to produce a yellow smoke.

Screening Smoke Compositions

Screening smoke compositions may be filled into ground candles for burning to make a smoke screen, or may be used in shells, bombs or grenades for the same purpose. White phosphorus is used in shell which burst on graze; Berger compositions are used for shell of the base ejection type.

The smoke used for screening objects is almost invariably white. It is generally generated by dispersing substances which absorb, or react with, the moisture in the air. Consequently, they form a better screen in moist than in dry air. The most common materials are white phosphorus, chlorsulphonic acid mixture and Berger compositions.

Phosphorus is by far the most effective smoke producer. White phosphorus (Chapter XI) is so readily ignited in air that shells containing it do not need any igniting composition, but this ready inflammability necessitates stores containing it being carefully segregated, and they may be carried on ships only as deck cargo.

On ignition, phosphorus burns with the formation of dense clouds of phosphorus pentoxide. At the same time, much heat is evolved (and phosphorus has therefore a useful incendiary effect).

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\substack{\text{Oxygen}\\ \text{(from air)}}}{50_2} \rightarrow \underset{\substack{\text{Phosphorus}\\ \text{pentoxide.}}}{P_4O_{10}} + 740\text{ K.}$$

Owing to this heat the air surrounding the dispersed phosphorus pentoxide becomes heated and ascends carrying the smoke particles with it. This effect, which is known as "pillaring," detracts from the otherwise excellent smoke-producing properties of white phosphorus. Phosphorus pentoxide readily attracts moisture from the air, to form phosphoric acid, and this action enhances considerably the cloud effect.

$$P_4O_{10} + 6\ H_2O \rightarrow \underset{\text{Phosphoric Acid.}}{4\ H_3PO_4}$$

The appearance, on burst, of a phosphorus smoke shell is very characteristic. A cloud immediately forms, and firebrands of burning phosphorus are seen. This subsidiary incendiary action may cause fires at the point of burst in very dry weather, and it has a considerable moral effect on personnel against whom the shell are employed, since burning phosphorus causes most unpleasant wounds. Owing to the "pillaring" effect, the smoke screen which develops is very tall over the point of origin, and becomes lower and thicker downwind of the point of origin, being at its thickest about 200 yards from this point, after which it gradually tails off and becomes negligible about 1,000 yards from the point of origin. It is the practice, therefore, to originate such clouds about 200 yards upwind of the place which is to be effectively screened.

Chlorsulphonic acid mixture ($Cl.SO_3H+SO_3$) was introduced by the Germans during the Great War. Their method of using it was to drop the mixture on to lime, when an exothermic reaction occurs :

$$\begin{array}{ccccc} 2Cl.SO_3H & +CaO & \rightarrow & 2SO_3+H_2O & +CaCl_2+\text{Heat} \\ \text{Chlorsulphonic acid} & \text{Lime} & & \text{Sulphur trioxide} & \text{Calcium Chloride} \end{array}$$

The resultant sulphur trioxide, together with the sulphur trioxide which was originally dissolved in the chlorsulphonic acid, is volatilized, and combined with moisture from the air, to form a white cloud composed of droplets of sulphuric acid :

$$SO_3+H_2O \rightarrow H_2SO_4+\text{Heat}$$

A similar cloud is formed when chlorsulphonic acid mixture is sprayed into the air from an aeroplane or from the exhaust pipe of a tank :

$$Cl.\ SO_3H+H_2O \rightarrow H_2SO_4+HCl.$$

Good white smoke clouds are obtained by spraying the volatile liquid tetrachlorides of titanium, tin (stannic chloride), silicon and certain other elements, or by scattering them with a small explosive charge. All these chlorides interact with the moisture of the air. The greater the humidity of the air, the better do these chlorides act as smoke-producers.

The Berger compositions depend, for their action, on the production of zinc chloride which is volatilized into the air by the heat of combustion of the mixture, and unites with the moisture in the air to give minute drops of zinc chloride solution.

The Berger compositions consist of a mixture of zinc powder, zinc oxide and a chlorinated hydrocarbon, such as carbon tetrachloride, tetrachloroethane, hexachloroethane, etc. Calcium silicide may also be added to increase the heat of combustion of the mixture.

A typical Berger composition is S.R.264A, which has the average composition :

Hexachloroethane, C_2Cl_6	45·0 parts
Zinc Oxide, ZnO	45·0
Calcium Silicide, $CaSi_2$	10·0±1
	100·0

The smoke is produced by the interaction of the zinc oxide and the hexachloroethane.

$$C_2Cl_6+3ZnO \rightarrow 3ZnCl_2+CO_2+CO$$

This reaction is induced by the heat produced by the combustion of the calcium silicide along with some of the hexachloroethane.

For addition to the fillings of certain high explosive shells, which give but little smoke on detonation, and as bursters for chemical shell, some mixtures have been introduced, which are both explosive and smoke producing; on the bursting of these shell, sufficient smoke is evolved for purposes of observation. Typical of these is Mixture, Explosive and Smoke No. 7, which has the composition :

	parts
Ammonium Nitrate	40
Ammonium chloride	40
T.N.T.	20
	100

Incendiary Compositions

Illuminating Compositions, which contain powdered aluminium or magnesium, produce a very high temperature on combustion. By modifying the proportions of the ingredients, this property can be accentuated, and the composition used for incendiary purposes.

Incendiary agents may be employed in aerial or trench-mortar bombs, or in shell. In the latter the incendiary composition, after ignition, is usually scattered by a small bursting charge. Some incendiary mixtures, such as thermite, are difficult to ignite, and must be initiated by a special priming composition.

An incendiary mixture should have either a very high temperature of combustion or a persistent flame effect. When ignited, it should be difficult to extinguish.

The following is a typical composition for the filling of a " carcass," or incendiary bomb, which is effective against readily inflammable material. It does *not* burn at a very high temperature, and the incendiary effect is dependent on the long flames produced.

Carcass Composition

	parts
Potassium nitrate	34
Sulphur	13·5
Resin	10
Antimony Sulphide	3·5
Russian tallow	3·5
Venice turpentine	3·5
Mealed powder	5
Aluminium powder	27
	100·0

For use against a less readily inflammable material, thermite (see Chapter I) is used as an incendiary agent.

Military Thermite

	parts
Hammer scale (Fe_3O_4)	76
Aluminium powder (or flake)	24
	100

On ignition, a vigorous reaction occurs. There is little gas and flame but a great evolution of heat, which is retained in the mixture of molten iron and aluminium oxide. The mixture may be scattered by a small bursting charge, and it has then a wider incendiary effect. If not scattered, the effect is local, owing to the absence of flame, but thin sheets of metal may be perforated by the extreme temperature of the molten material.

Cendite

This is a modification of thermite, which burns with a longer flame, and is easier to ignite. The aluminium is protected from corrosion by coating it with boiled linseed oil. The composition of cendite is :

	parts
Aluminium powder	18
Boiled linseed oil	3
Hammer scale	44
Barium nitrate	35
	100

J.—SAFETY PRECAUTIONS

CHAPTER XXIV

SAFETY PRECAUTIONS

See also Magazine Regulations, Parts I and II (1934) (Land Services).

Introduction.

Throughout the manufacture, packing, storage and handling of explosives, precautions have to be taken to avoid accidents, the results of which may be disastrous to life and property. The storage and handling of finished explosives and the precautions to be observed are laid down as far as the Service is concerned in Magazine Regulations; for the guidance of the public in general, regulations are drawn up by the Home Office. It is proposed in this chapter to give a general résumé of the precautions necessary in the manufacture of explosives, with the intention of emphasizing the reasons underlying them. The general principles then become evident, and an informed and intelligent understanding can then be brought to bear on the regulations laid down in other publications.

Buildings.

These may be broadly divided into two main classes; buildings in which the manufacture of some explosive is carried out, and magazines or buildings in which explosives are stored.

1. The danger of explosion is greater in the first case. Therefore, the building should be of such a nature that in the event of an explosion taking place within it, the effects are confined to that building and not transmitted to its neighbours.

With that end in view, such buildings are made on as light and flimsy a scale as possible. Weighty masses are avoided as they may be projected to a considerable distance by an explosion. For the walls, light fire-resistant material is usually employed, and for the roof, corrugated iron. The flooring is usually made of asphalt, or lead sheeting joined together by burning. The whole of the interior should be constructed with regard to the avoidance of cracks and crevices in which explosive material may lodge.

All doors are made to push open outwards, and are sited on the lines of exit which workers would be most likely to take in an emergency.

Mention has been made of the use of corrugated iron for roofing. It is not entirely satisfactory, and other materials such as

" Ruberoid " have been tried. Tarred felting and any material of that nature is useless as it is very inflammable. " Ruberoid " suffers from that disadvantage, but it is readily extinguished if it is projected through the air. The roof should be as light as possible, though this involves a risk of the roof being penetrated by heavy debris from an explosion in the vicinity.

Wood may often be used in the construction of these buildings, particularly where picric acid or picrates are present. It should be avoided in nitric acid factories or stores containing nitrates, as wood impregnated with these substances is very inflammable and burns fiercely.

Exposed ironwork should be avoided as a general rule ; this is imperative where sensitive explosives are being handled.

Lead, iron, lime or whitening must on no account be present in buildings containing picric acid or its derivatives, on account of the danger of the formation of sensitive picrates.

Paints must be lead-free. Titanium or zinc oxide paints are preferable. Paints containing grit or silica must be avoided.

Where nitroglycerine or its vapour are present, buildings should not be lined, as this explosive may accumulate behind the lining.

Nails or screws entering into the construction of buildings, except those containing ammonium nitrate, should be of copper or brass. If they are made of steel or iron they should be countersunk and the heads covered with putty.

2. In magazines or stores the danger of explosion is not nearly so great, and the risk of unauthorized entry is the paramount consideration. A much stronger method of construction must therefore be adopted, though this is not necessary in places guarded by police or watchmen during the absence of the workers.

Distances between buildings

For buildings under civilian control, regulations have been drawn up by H.M. Inspectors of Explosives laying down the minimum distance permissible between adjacent buildings containing explosives. These distances depend upon :

(*a*) Whether the explosives contained in the buildings bear a fire risk, or an explosive risk, or both.

(*b*) The presence of intervening ground either as natural or artificial mounds.

(*c*) The quantity of explosive which the contiguous buildings are designed to contain.

Other countries have similar regulations, though the distances are governed by different considerations, in some cases being based on the results of tests. In the United States a detailed study was made of the effects of accidental explosions in all parts of the world, and a quantity-distance table was drawn up defining the minimum safe distances between magazines and inhabited buildings.

In France an extended series of experiments was carried out, and a formula connecting distance with weight of explosive was evolved. It was found that for a given effect, the distance from an explosion, at which this effect might be expected, varied as the square root of the weight of explosive present, *i.e.* $d=k\sqrt{w}$, where

d=distance in metres,
w=weight of explosive in kilograms,
k=a constant which depends on the nature of the explosive, the kind of effect considered, and the existence or absence of earth traverses. It varies in value from 15 to $2\frac{1}{2}$.

It is questionable whether this theory can be applied to all practical cases, particularly where large masses of explosives are involved.

For instance, the rate of explosion of gunpowder is comparatively slow. It therefore will do most damage where the resistance offered to it is least, *i.e.* the walls and roof of a building will suffer more than the ground beneath it. With high explosives this is not the case. The rate of explosion is very much greater, and the air offers considerable resistance, and acts as a tamping, with the result that high explosives have the appearance of striking downwards.

Explosions of such materials as nitroglycerine are very violent, and concussion waves are set up, both in the air, and in the ground. The latter are usually the more feeble, as the explosive is usually insulated from the ground to some extent by the packing in which it is contained, and the platform by which it is supported. Consequently, the air wave is the more violent and causes the most damage. That this is so is evidenced by the protection afforded by earth mounds, which can only intercept the air wave, and can have little or no effect on the ground wave. The effect of these mounds is to reduce the damage by at least one-half.

In the British Services, safety distances proportional to the square root of the weight of explosive have also been adopted. A distinction is drawn between "outside" and "inside" distances. Outside distances are the distances which must separate the magazines of a depôt from inhabited buildings, public highways, etc., situated outside the depôt in order to safeguard life and property in the event of an explosion. Inside distances are the distances between the magazines within the depôt, and are such as to ensure that an explosion or fire in one magazine is not propagated to an adjacent one. The safety distances depend on the type of explosive or ammunition stored. For material which is liable to detonate *en masse* the distances are calculated from the formulæ

$d=110\sqrt{w}$ for the outside distances
$d=11\sqrt{w}$ for the inside distances

where d is the distance in yards and w is the number of thousands of pounds of explosive. Thus, for 150,000 lb. of explosive the outside distance is $110\sqrt{150}=1350$ yards, and the inside distance is $11\sqrt{150}=135$ yards. If the stores contain only ammunition and explosives which, while subject to an explosion risk, are not liable to detonate *en masse*, the above safety distances may be reduced by one-half for the outside distances and by one-quarter for the inside distances. For material bearing a fire risk only, a further reduction of the distances is permitted.

These safety distances apply to magazines and storehouses which are traversed all round up to the eaves by a substantial mound, or, alternatively, are adequately screened by natural undulations of the ground. If protection of this type is not provided, either the safety distances must be doubled, or the explosive limit reduced to one quarter.

The Service requirements outlined above for the safe spacing of magazines and explosives storehouses refer to buildings situated above ground. For stores constructed with sufficient overhead cover to render them bomb-proof reduced safety distances are permissible compared with traversed magazines of the same content and capacity.

Detonators and detonating or cap compositions may be fired by electro-magnetic induction from a high-power wireless station.

The safety distance from a high-power wireless station is given by the formula :

$d=500\sqrt[3]{p}$ where d=distance in yards,
p=power of station in kilowatts.

Thus for an 8-k.w. station

$$d=500\sqrt[3]{8}=1,000 \text{ yards.}$$

Lighting of buildings.

All windows and skylights are made, as a rule, of glass with a wire insertion, so as to prevent the ingress of debris. Windows, except those facing north, are dulled in some way, so as to protect the contents of the building from direct sunlight, which has a deleterious effect on most explosives. Non-actinic glass is desirable.

For artificial lighting, electric lamps are almost always employed. They are preferably mounted in such a manner that all switches, connections and wiring are outside the building, and it is usual to find the lamps outside and placed so that they illuminate the building through a window. If they are inside, they should be well protected by strong outer globes. All circuits should contain double pole switches with a fuze in each branch of the circuit.

For magazines or buildings where explosives are only present in packages, lamps burning rape oil or candles may be used, but they should be mounted in recesses in the wall which are glazed on the inside. Access to the lamps should only be from the exterior of the buildings.

For portable lamps, electric torches are preferable, though in some cases portable candle lamps may be permitted.

Precautions against lightning.

Lightning can be dangerous to buildings containing explosives in two ways :

(*a*) The building may be directly struck and so destroyed.

(*b*) A flash may strike near a building and induced currents, set up by it in the metal work of the structure, may give rise to a spark and so cause an explosion.

The precautions to be taken are therefore twofold, and the best system is probably that described below.

1. Plain metal masts should be sited at some little distance from the building, and well " earthed." They should be provided with a sharp point at the top, as this assists in the dissipation of the electrical charge induced in the earth's surface by the passage of a thunderstorm over it.

In dry ground, arrangements are usually provided to ensure good conductivity between the mast and the ground by drenching the base.

Lightning conductors must be straight, *not* kinked, as a " strike " will probably short circuit a kink.

2. Metal portions of the structure should be bonded together and earthed, and metal objects in the building should be connected either to the main structure or to a separate earth connexion.

The above precautions for the prevention of explosion by lightning are particularly necessary in the case of nitroglycerine nitrating houses, since these buildings contain large masses of metal, and are necessarily situated at the highest point of a factory site.

Electrostatic charges.

These charges accumulate, and may result in sparking, in many processes. Belts driving incorporators in cordite manufacture may be charged by the friction of driving. Frequent dressing with glycerine and water removes this danger by increasing the conductivity of the belt. Modern factories eliminate this danger by adopting direct drive, employing electric motors. The motors are housed outside the compartment containing the explosive, the driving shaft passing through the partition. Dry nitrocellulose is very liable to electrification. For this reason all racks or boxes in which this explosive may be stored should be thoroughly connected to earth.

" Clean " areas.

Barriers are erected at all entrances to danger buildings, at which all persons are required to change their footwear for special boots, or in the case of visitors, to don overshoes. A raised part of the " clean " floor is provided on which the special boots or overshoes stand. A division is made between the " clean " and " dirty " areas by means of a board about 9 inches high, and in addition, the " clean " area is often outlined in red, or indicated in some other manner.

The boots or overshoes are rubber soled, and in some cases, such as for workers handling dry nitrocellulose, copper rivets are placed in the sole so as electrically to " earth " the wearer.

The regular employees are provided with special clothing, which has no pockets, and no metal buttons or fastenings. Steps are taken to ensure that this clothing does not become saturated with explosive or inflammable material.

All persons entering a danger area are also required to deposit all smoking materials and combustibles, such as pipes, matches, tobacco, cigarettes, pocket lighters, etc., at the entrance. This provision is enforced by giving some principal official the right to search or to authorize the search of any persons in a danger area.

Thawing of frozen explosives.

In countries in which low temperatures prevail in the winter, nitroglycerine explosives may become frozen and require thawing. This is best done in special thaw houses, in which the temperature is maintained at about 38° C. by external hot-water pipes. The ideal method is to eliminate the danger of freezing by keeping the magazines and buildings at a temperature of 15°–20° C. winter and summer.

Tropical storage

Hot, damp conditions of storage are exceedingly detrimental to the stability of most explosives (an important exception is picric acid), and so precautions are particularly necessary in tropical climates to ensure the coolness and thorough ventilation of magazines. Storage is considered to be " tropical " where the average daily temperature throughout the year exceeds 75° F. If the buildings are solidly constructed, and well covered with earth, the temperature does not vary sensibly throughout the twenty-four hours. Ventilation should only be allowed when the temperature of the outside air is at its lowest, *i.e.* at night or in the very early morning.

If large quantities of explosives are being stored, cooling with water from refrigerators should be employed, with the assistance of thermal insulation of the walls, floor and roof.

Spontaneous ignition and explosions.

No case has yet been recorded of smokeless powders, of themselves, exploding after spontaneous ignition. But fires of this nature have been accompanied by phenomena of a distinctly explosive nature which have been traced to the explosion of combustible gases evolved during the burning of the propellant. That such gases are given off under these conditions was demonstrated by Berthelot. He ignited nitroglycerine and nitrocellulose under a pressure of approximately one atmosphere, and analysed the products of combustion. The following are his figures :

Gas	Nitroglycerine	Nitrocellulose
NO	48·2	24·7
CO	35·9	41·9
CO_2	12·7	18·4
H_2	1·6	7·9
N_2	1·3	5·8
CH_4	0·3	1·3
	100·0	100·0

It must be remembered that this analysis only holds good for the conditions under which the combustion took place, and that factors such as degree of confinement, temperature, amount of air present, etc., will all have their effect in any particular instance. But it is safe to presume, from the foregoing, that there will always be present an appreciable quantity of combustible gases which will mix with air to form an explosive mixture.

The result of the spontaneous ignition of a smokeless powder is therefore rendered more dangerous by the risk it entails of a gas explosion. This gas explosion may be sufficiently violent to break down partitions, and so cause the ignition of explosives stored in adjacent compartments. An adequate distance must therefore be maintained between buildings containing smokeless powder, though less separation is necessary than with high explosives.

The action of stabilizers in retarding the decomposition of these explosives has been discussed in another chapter. From the point of view of this chapter, the maintenance of moderate temperatures in buildings is the best precaution against spontaneous ignition.

While it is true that explosion does not, as a rule, follow the ignition of smokeless powders and kindred explosives, it must be remembered that if the explosive is in small sizes and in large quantities the combustion can become very violent. The danger lies in the possibility of the fire spreading to other explosives which will explode on ignition.

Repair of buildings.

Before any repairs are carried out on a danger building (except in the case of minor repairs to the exterior of a building), all explosives should be removed from it, and the whole structure thoroughly cleaned out and afterwards inspected. All spaces, corners and crevices where any explosive material may have lodged should have careful attention paid to them. Any portion of the building which has become saturated with explosive should be replaced.

No material should be used for cleaning purposes which will have a deleterious effect on explosives.

K.—APPENDICES.

APPENDIX I

BIBLIOGRAPHY

The following publications will be of use to the reader who is desirous of obtaining fuller knowledge of some of the applications of explosives and of matters and processes which had, perforce, to receive brief mention in this textbook. This bibliography is *not* intended to be exhaustive; it merely gives a representative selection of relevant publications.

Military Publications

H.M.S.O. = His Majesty's Stationery Office.
~~F.O.U.O. = For Official Use Only.~~
N.T.B.P. - Not to be published.

(1) Textbook of Anti-Aircraft Gunnery, Vol. I. ~~F.O.U.O.~~ N.T.B.P., H.M.S.O. (For account of compositions for use in time fuzes.)

am 1 (2) Textbook of Ammunition. H.M.S.O., 1936. ~~F.O.U.O.~~ N.T.B.P.

(3) Magazine Regulations. Parts I and II. Land Service, 1934. N.T.B.P. ~~F.O.U.O.~~, H.M.S.O.

(4) Armament Training Manual of the Royal Air Force, Part II. NTBP. ~~F.O.U.O.~~ Air Publication 1243. Air Ministry, 1927. (*See* Chapter V for Pyrotechnic Compositions.)

(5) Military Engineering, Vol. IV. (Mining and Demolitions.) H.M.S.O.

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(10) A. Marshall: Explosives. Vols. I and II, 1917. Vols. III, 1933. Churchill and Co.

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(12) Vennin et Chesneau: Les Poudres et Explosifs. Paris, 1932. (Pages 322 *et seq*. give an account of the Schmid Process for making nitroglycerine.)

(13) A. Marshall: Dictionary of Explosives. Churchill, 1920.

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(16) Professor T. Martin Lowry: Inorganic Chemistry. MacMillan.

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(19) Hilditch: Catalytic Processes in Applied Chemistry. Chapman and Hall, 1929.

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(21) G. W. C. Kaye and T. H. Laby: Physical and Chemical Constants. Longmans, Green and Co., Ltd., 1936.

APPENDIX II.

Table II.A—Physical Constants for Explosives.

NOTE. The (small) gram-calorie is used in this Table. P/A = Picric Acid.

Explosive	Specific Gravity at 15·5°C.	Figure of* Insensitiveness P/A = 100	N in N/C average per cent.	Ignition Point °C.	Volume of Total Gases (c.c./gram)	Heat of Decomposition (gram cals/gram-water gaseous)
Propellants						
1. Ballistite 40/60 ...	1·6	25	12·6	166	830	1135
2. Cordite Mk. I ...	1·57	70	13·1	151	885	1125
3. ,, M.D. and M.C.	1·58	56	13·1	160	935	940
4. ,, R.D.B. ...	1·54	61	12·2	155	960	915
5. ,, W	1·60	40	13·1	153	935	945
6. ,, S.C. ...	1·57	40	12·2	154	940	900
7. N.C.Z.	1·6	30–40	13·0 Made up of 35% of 12·6 and 65% of 13·2	165	930	815
8. Gunpowder (Former Propellant classed here for convenience)	1·65–1·85	90	Not applicable	above 250	255	725

* NOTE: Propellants in cord form are considerably safer than the figure of insensitiveness indicates.

Table II.A (*continued*)—High Explosives.

Explosive	Specific Gravity at 15·5° C.	Figure of Insensitiveness P/A =100	Rate of Detonation in metres/sec. at density	Melting Point °C.	Ignition Point °C.	Volume of Total Gases (c.c./gm.) at density	Heat of Decomposition (gm. cals./gm. water Gaseous) at density
1. Amatol 40/60	1·70	115	6470 (1·55)	76–80	240	890 (1·54)	920 (1·54)
2. Amatol 80/20	1·71	111 to 120	5080 (1·3)	—	235	900 (1·45	920 (1·45)
3. Ammonal	—	over 110	4100 (1·07)	—	above 250	900 (1·1)	1400 (1·1)
4. Baratol 70/30	2·57	100	4100 (2·42)	—	240	380 *	760 *
5. Baratol 20/80	1·86	101	4600 (1·09)	76–80	285	650 *	910 *
6. Dinitrophenol	1·68	over 120	6400 (1·62) 6120 (1·56)	110–114	above 250	730 *	780 *
7. Guncotton (Dry)	1·67	23	7300 (1·15)	—	187	850 (1·15)	960 (1·15)
8. Guncotton (wet) 13% water ...	—	70–100	5500 (1·23)	—	187	900 (1·2)	750 (1·2)
9. Lead azide	4·81	15 to 25	4500 (3·8)	—	above 250	230 (4·01)	385 (4·01)
10. Lead Styphnate	3·09	18	4900 (2·6)	—	above 250	325 (2·93)	450 (2·93)
11. Lyddite (fused T.N.P.) ...	1·76	100	7250 (1·63)	121·6	above 250	700 (1·6)	990 (1·6)
12. Mercury Fulminate	4·43	10	4500 (3·3)	—	160	230 (4·07)	410 (4·07)
13. Nitroglycerine	1·6	13	7500–8000 (1·6)	13	188	713 (1·6)	1478 (1·6)
14. Picric Powder	—	85–87	—	—	above 250	748 *	722 *
15. Tetryl (C.E.)	1·76	70	7520 (1·45)	129	180	930 (<1·1) 830 (1·1–1·3) 760 (1·4–1·76)	910 (<1·1) 1020 (1·1–1·3) 1110 (1·4–1·76)
16. Trotyl (T.N.T.)	1·68	106 to 115	6950 (1·57)	76–80	240	640 (1·56)	1040 (1·56)

* Estimated.

Table II.B—Results of Pressure Bar Measurements.

Explosives	Weight	Density	Container	Shaft Protection (Asbestos pellet)		Pressure Tons/sq. in.
				Length	Density	
1. Amatol 40/60 ...	48·1 grams	Cast	Bomb, ¼-in. wall, with cap	1·55″	1·3	41·9
2. Amatol 80/20 ...	47·3 grams	1·3	do.	,,	,,	36·9
3. Amatol 80/20 ...	41·7 grams	1·2	Paper	,,	,,	10·8
4. C.E. Grade I ...	47·3 grams	1·3	Bomb, ¼-in. wall, with cap	,,	,,	46·2
5. Gunpowder ...	51 grams	1·45	do.	,,	,,	8·2
6. Lead azide. With 6.6.4. composition	3¼ grains lead azide 1½ grains 6.6.4.	Pressed at 1000 lb. dead load Pressed at 900 lb. dead load	5-grain shell, in brass collar	0·197″ (5 mm.)	1·25	9·3
7. Lyddite ...	47·3 grams	1·3	Bomb, ¼-in. wall, with cap	1·55″	1·3	45·3
8. Lyddite ...	41·7 grams	1·2	Paper	,,	,,	11·85
9. Mercury fulminate	4 grains	Pressed at 1000 lb. dead load	4-grain shell, in brass collar	0·197″ (5 mm.)	1·25	10·7
10. Do.	5 grains	do. do.	5-grain do.	,,	,,	12·3
11. T.N.T. Grade I	47·3 grams	1·3	Bomb, ¼-in. wall, with cap	1·55″	1·3	42·3
12. Do.	41·7 grams	1·2	Paper	,,	,,	13·2

APPENDIX III

GLOSSARY OF TERMS

Analysis. (Greek *ana*=up; *luein*=to loosen.) This is the process whereby the composition of a substance is determined. *Qualitative* analysis consists in finding out the nature of a compound or mixture by the application of physical and chemical tests. *Quantitative* analysis consists, when the nature of a substance has been determined, in ascertaining the proportion in which its constituent compounds or elements are present. An example will serve to make this clear:

The high-explosive filling of a captured enemy shell was a whitish powder. It was required to know the nature of this powder. The chemist, to whom the sample was given, proceeded thus:

(i) *Qualitative analysis.* The powder was found to consist of two constituents, one of which was completely soluble in water; the other insoluble in water, but soluble in benzene. The aqueous solution was subjected to chemical tests, and found to contain ammonium nitrate only. The portion which was insoluble in water was found to be a pale yellow crystalline solid, which melted at 81·5° C. This suggested that the substance was T.N.T.; a surmise which was verified by chemical tests.

The mixture therefore, consisted of ammonium nitrate and T.N.T. (an amatol).

(ii) *Quantitative analysis of the substance.* This was undertaken in order to determine the percentages of T.N.T. and of ammonium nitrate in the mixture.

A weighed amount of the substance was extracted with water, the residue of T.N.T. collected by filtration on a tared filter paper, dried in a steam oven, and weighed. From the weight of T.N.T. the percentage of T.N.T. in the mixture was calculated. The percentage of ammonium nitrate was got by difference and checked by repeating the extraction, using benzene in which T.N.T. is soluble, but ammonium nitrate insoluble.

Absolute temperature. (*See* **Temperature, Absolute.**)

Autoclave (Greek *auto*=self; Latin *clavis*=a key. Lit. a self-closing vessel). A vessel capable of withstanding internal pressure, in which a chemical process can be performed at temperatures higher than the normal boiling-point of the materials taking part in the process.

Calorie. Throughout this book the kilogram calorie is used, and this is defined as the amount of heat required to raise 1 kilogram of water from 15° to 16° C. It is denoted throughout by the symbol K.

Catalyst (Greek *kata*=down; *luein*=to loosen). A substance which accelerates a chemical action, but is itself unchanged at the *end* of the process, though it *may* form chemical compounds with the reacting substances during the reaction.

Catalytic action. The operation of a catalyst.

The German physical chemist Ostwald compared a catalyst with a lubricating oil. The following comparison is based on Ostwald's dictum:

(i) The oil does not stop or start the machine; it merely facilitates its working. Similarly, catalysts do not stop or start reactions; they merely accelerate a reaction which can already take place, though very slowly indeed.

(ii) Heavy engine oil would not be used to oil a watch; similarly, certain catalysts assist certain reactions, *i.e.* the action of a catalyst is specific in its nature.

(iii) The oiling of a machine does not alter its velocity ratio. Similarly, the addition of a catalyst does not alter the proportions of the end-products of a reaction.

(iv) Grit in the bearings of a machine will interfere with its proper functioning, even if the correct lubricant has been applied. Similarly, a catalyst may be " poisoned " by the presence of certain substances. Thus arsenic must be carefully removed from the sulphur dioxide—air mixture before it is passed over the platinum catalyst in the Tenteleew Contact Process for making Sulphuric Acid (Chapter X) as arsenic " poisons " the catalyst.

Centrifuge. A machine used for separating liquids from solids by the action of centrifugal force. The substances are contained in a perforated cylindrical vessel which can be rotated at a high speed. The liquid is driven through the perforations to the outside, whence it may be withdrawn. A familiar example of a centrifuge is the centrifugal drier used in laundries.

Colloids. The term " colloid " has been used in connection with cordite, so a brief account of colloids is here appended.

In 1861, Graham investigated the rates of diffusion, through parchment membranes, of aqueous solutions of various substances. As a result of his experiments, he divided soluble substances into two types:

(*a*) *Crystalloids*. Solutions of which showed rapid diffusion; for example, sodium chloride, NaCl.

(*b*) *Colloids* (Greek *kollos*=glue). Solutions of which show slow or zero diffusion, *e.g.* gelatine, silicic acid.

The modern view, however, is that colloids are not distinct substances, but that the colloidal state is a form into which most matter can be brought. Thus sodium chloride, a typical crystalloid, can, by suitable means, be brought into the colloidal state. Conversely, egg albumen, a typical colloid, can be obtained in the crystalline form.

In true solutions, the particles of solute are of molecular size. In colloidal solutions, the solute is dispersed in larger aggregates. In the extreme, a colloidal solution merges into a coarse suspension, as of mud in river water.

Colloidal solutions (*Sols*) can be coagulated to a *gel* by various means, *e.g.* by heat, acids, bases and salts. A colloid which can be redissolved after coagulation is termed a *reversible colloid* (*e.g.* gelatine); one which cannot so be redissolved is termed an *irreversible colloid*, *e.g.* egg-albumen (white of egg), after coagulation by boiling.

The " solute " in a colloidal solution is termed the " disperse phase "; the solvent " the dispersion medium ". The following list shows the types of colloidal solution.

Disperse Phase	*Dispersion Medium*	*Name*
Solid	Liquid	Sol.
Liquid	Liquid	Emulsion
Gas	Liquid	Foam
Solid	Solid	Solid solution
Solid	Gas	Smoke
Liquid	Gas	Fog
Gas	Gas	Non-existent, as gases mix in all proportions

Counter-current Methods. Methods by which two fluids may be caused to interact while flowing in opposite directions, *i.e.* counter-current. The products of their interaction follow the direction of flow of their parent substance. Thus in the Oldbury process of nitrating M.N.T. to T.N.T. described in Chapter XVIII, the M.N.T. is gradually nitrated to T.N.T., the direction of flow remaining the same as that of the original M.N.T. The nitrating acids flow continuously in the opposite direction to the nitro-body, becoming progressively weaker, until they emerge as waste acid at the M.N.T. end of the plant.

Apart from the incidental saving in time, plant and labour, they possess a distinct technical advantage in that the last stages of the reaction are performed by the reagents in their most concentrated form.

Density of loading. The ratio :

$$\frac{\text{Weight of charge in the chamber (in grams).}}{\text{Weight of water which would fill the chamber (in grams)}}.$$

The denominator is equivalent to the volume of the chamber in cubic centimetres.

Deliquescence. The property possessed by some substances of dissolving in moisture absorbed by them from the air, *e.g.* calcium chloride ($CaCl_2$).

Distillation, Fractional. The separation of a mixture of two or more liquids by heating the mixture at temperatures rising successively through their various boiling-points. The vapour that comes over at each boiling-point is condensed and contains the majority of the constituent which boils at that temperature. The mixture is thus separated into fractions. The fractions may be further purified by repeating the process.

By the adoption of special stills, mixtures of liquids whose boiling-points are very close together may be separated at one operation.

An example of fractional distillation is the recovery of acetone from the acetone-water mixture which results from the purification of tetryl (Chapter XIX).

Distillation Steam. Substances which would char if heated strongly but which vaporize slowly at the temperature of boiling water, may often be distilled by passing a current of steam through them. The steam carries with it the vaporized substance, which can then be recovered by condensation. This process is known as *steam distillation*.

Endothermic action. A chemical action in which heat is absorbed. An example is the decomposition of ammonium carbonate by heat (Chapter I).

Endothermic compound. A compound which absorbs heat on its formation. An example is lead azide.

Exothermic action. A chemical action in which heat is liberated. An example is the thermite reaction (Chapter I).

Exothermic compound. A compound, during whose formation heat is liberated. Water is an example :

$$2H_2+O_2 \rightarrow 2H_2O \text{ (gaseous)} + 2\times 58\text{K}$$

Ester. The organic analogue of a salt, which is formed from an acid (organic or inorganic) and an alcohol. Compare the formation of inorganic salts.

Examples :

(i) Inorganic salt

$NaOH$	+	HCl	→	$NaCl$	+	H_2O
Caustic soda		Hydrochloric acid		Common salt		water

(ii) Esters

(*a*) $C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$

Ethyl alcohol — Ester (ethyl chloride)

(*b*) $C_2H_5OH + CH_3COOH \rightarrow CH_3CO.OC_2H_5 + H_2O$

Acetic acid — Ethyl acetate (acetic ester)

(*c*)

$$\begin{array}{l} CH_2OH \quad HNO_3 \\ | \\ CH\ OH + HNO_3 \\ | \\ CH_2OH \quad HNO_3 \end{array} \rightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CH\ ONO_2 . + 3H_2O \\ | \\ CH_2ONO_2 \end{array}$$

Glycerol. Nitric acid — Ester glyceryl trinitrate (N./G.)

Eutectic. A mixture of two or more substances, which has the lowest melting-point of any possible mixture of the constituents, and in which the components are structurally distinct. Thus water freezes at 0° C., common salt at 801° C., but their eutectic freezes at $-22°$ C.

Fractional distillation. See **Distillation, Fractional.**

Gram-molecule. The molecular weight, in grams, of a substance. Thus the gram-molecule of water, H_2O, is 2×1 (Hydrogen) $+ 16$ (Oxygen) $= 18$ grams.

Hydrolysis. A particular case of chemical decomposition in which the elements of water are added to a substance, followed by splitting into an acid and a hydroxy compound. For example :

$$TiCl_4 + 4H_2O \rightarrow 4HCl + Ti(OH)_4$$

Titanium tetrachloride — Titanic acid

Where an alkali is used, instead of water, to hydrolyze an ester, the process is called saponification, the word being derived from the soap-boiling process (Chapter VII). Thus :

$$C_3H_5(O.OC.C_{17}H_{35})_3 + 3NaOH \rightarrow 3C_{17}H_{35}.COONa + C_3H_5(OH)_3$$

Glyceryl stearate or tristearin — Sodium stearate (soap) — Glycerol

Hygroscopic. A substance capable of absorbing moisture from the air and retaining it is said to be hygroscopic, *e.g.* ammonium nitrate.

Isomeric. (Greek *isos* = equal ; *meros* = a share). Having the same molecular formula, but possessing different chemical and physical properties owing to a difference in the structure of the molecule. Substances so related to each other are known as isomers. Isomerism may be either :

(i) Structural isomerism. Example :

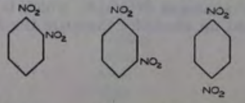
C_2H_6O is the molecular formula of both :

(*a*) Ethyl alcohol CH_3-CH_2-OH

(*b*) Dimethyl ether CH_3-O-CH_3

These differ completely both in chemical and physical properties.

(ii) Position isomerism. Example, the D.N.B's.

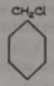


Ortho- Meta- Para-dinitrobenzene

These have somewhat similar chemical properties, but differ in physical properties, especially as regards melting-point.

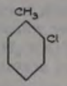
Structural and position isomerism may occur together. Thus : C_7H_7Cl is :

(*a*)



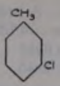
Benzyl chloride

(*b*)



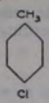
Ortho-

(*c*)



Meta-

(*d*)



Para-chlorotoluene

Kilowatt-hour. An electrical unit of work or energy.

The Board of Trade Unit (B.T.U.) is the kilowatt-hour and is equivalent to the energy that would be expended by a power of 1 kilowatt acting for 1 hour.

A kilowatt is 1·34 horse-power.

Molecular heat of formation. The amount of heat, measured in calories, given out or absorbed in the formation of 1 gram-molecule of a substance from its elements.

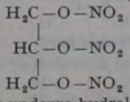
Molecular heat of combustion. The amount of heat, measured in calories, given out by the combustion of 1 gram-molecule of a substance when burnt in an excess of oxygen.

Molecular heat of explosion or decomposition. The amount of heat, measured in calories, given out by the decomposition or explosion of 1 gram-molecule of a substance in the absence of additional oxygen. With explosives which do not contain sufficient oxygen to convert all the carbon to carbon dioxide and all the hydrogen to water, the heat of explosion is less than the heat of combustion.

In practical determinations of the heat of explosion, the heat evolved is measured with the products of explosion reduced to normal temperature, *i.e.* any water produced is in the liquid state. To obtain the heat actually emitted by the explosion, in which the water is of course gaseous, a correction must be made for the latent heat of vaporization of the amount of water produced.

Mother liquor. The impure liquid remaining after a substance has crystallized out of solution.

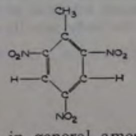
Nitrate, nitric ester. A compound formed by the action of nitric acid upon a substance, in which a hydroxyl group ($-OH$) is replaced by the nitrate group ($-O.NO_2$). In organic chemistry, nitric *esters* are distinguished from *nitro-compounds* by the linkage of the nitrogen to carbon through an oxygen atom, *e.g.* glyceryl trinitrate or nitroglycerine :



$$\begin{array}{l} H_2C-O-NO_2 \\ \quad | \\ HC-O-NO_2 \\ \quad | \\ H_2C-O-NO_2 \end{array}$$

These compounds readily undergo hydrolysis.

Nitro-compound, nitro-body. Compounds in which the nitro group ($-NO_2$) is introduced by replacement, usually of hydrogen. In organic *nitro-compounds*, the nitrogen is linked directly to carbon, *e.g.* tri-nitrotoluene :



Nitro-compounds are not in general amenable to hydrolysis. Certain nitro-compounds, which contain nitro groups in the ortho-position to one another, such as the unsymmetrical forms of T.N.T., can, however, be hydrolyzed.

Reversible reaction. A reaction which may proceed in either of two directions according to the conditions under which it is performed, *e.g.*

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Ethyl acetate (acetic ester)}}{CH_3COOC_2H_5 + H_2O}$$

The double reversed arrows indicate a reversible reaction.

(i) The reaction proceeds almost quantitatively from left to right if sulphuric acid be added to remove the water which is formed on esterification, or if excess of alcohol, or acid be present.

(ii) The reaction proceeds readily from right to left if excess of water be present or if caustic soda be added to neutralize the acetic acid as it is formed.

Saponification. (*See* **Hydrolysis.**)

Specific heat. The amount of heat required to raise unit mass of a substance through unit interval of temperature. If measured in calories, it is the amount of heat required to raise one kilogram of a substance through 1° C. With gases there are two principal specific heats, according as the determination is made at constant pressure (Cp) or at constant volume (Cv); the ratio Cp/Cv is an important physical constant of the gas, and is denoted by the Greek letter γ (gamma).

Steam distillation. See **Distillation, steam.**

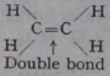
Synthesis. The formation of a substance from its elements, or by artificial methods, as distinct from its production from natural sources, *e.g.* synthesis of ammonia from nitrogen and hydrogen (Chapter IX) as distinct from the production of ammonia by the destructive distillation of coal.

Temperature, absolute. The *absolute zero* of temperature is that temperature at which the kinetic energy of all molecules is zero or at which a "perfect" gas would occupy zero volume. Absolute zero is −273·1° C. (−459° F.). Its value is based on the behaviour of gases, and on Lord Kelvin's thermodynamical arguments.

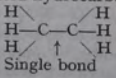
Unsaturated compounds. Compounds which are capable of combining with other compounds or elements by addition, there being no formation of substitution products, *e.g.*

$$\underset{\text{Ethylene}\quad\text{Chlorine}}{H_2C{=}CH_2 + Cl_2} \rightarrow \underset{\text{Ethylene chloride}}{ClH_2.C{-}CH_2Cl}$$

Unsaturated compounds contain a *double bond* in the molecule; thus ethylene is



while the corresponding saturated hydrocarbon ethane is



Water equivalent of a body. The mass of water which can be raised through a given interval of temperature by the amount of heat required to raise the body through the same interval of temperature. Numerically, it is the product of the mass of the body into its specific heat.

APPENDIX IV.

A SHORT DICTIONARY OF EXPLOSIVES

(*See also* Bibliography (Appendix I), and Chapter XX.

Ammonite. A coal-mine explosive. A modern variety of this explosive has the following composition :

Ammonium nitrate	79·5
Trinitro-naphthalene	5·5
Sodium chloride	15

The use of trinitro-naphthalene should be noted.

Antifrost, Polar, Eversoft, Arctic, North Pole and similar prefixes imply that an ingredient has been added to prevent freezing.

Bellite. A name formerly given to a mixture of ammonium nitrate and dinitrobenzene.

Blastine. A high explosive, which possesses the disadvantage of producing poisonous fumes of hydrochloric acid on explosion.

Ammonium perchlorate	60
Sodium nitrate	23
Dinitro-toluene	11
Paraffin wax	6

Carbo-dynamite. This explosive, though unimportant, is interesting. It differs from ordinary dynamite in employing cork charcoal instead of kieselguhr as the absorbent for the nitroglycerine ; 1 part of charcoal absorbs 9 parts of nitroglycerine.

Cheddite. A French chlorate explosive with the following composition :

Potassium chlorate	79
Castor oil	5
Mononitro-naphthalene	1
Dinitro-toluene	15

Cheesa sticks are used in South Africa as fuzes for blasting charges. They consist of sticks of cordite coated with powdered ammonium oxalate and shellac.

Dinitro-chlor-hydrin. $CH_2Cl.CH(NO_3)CH_2(NO_3)$. A yellow liquid with a slight aromatic smell. It is soluble in most organic solvents, but is insoluble in water and acids. It is less sensitive to blows and friction than nitroglycerine, but it is easily detonated by means of a fulminate detonator. It mixes with nitroglycerine in all proportions. It has a melting-point of about 2° C., and boils at about 192° C. It is useful as an " anti-freeze " for nitroglycerine.

Du Pont smokeless powder. An American shot-gun powder.

Soluble nitrocellulose	95·8
Metallic nitrates	2·2
Moisture	2·0

E.C. Powder. A successful smokeless powder for use in shot-guns.

Soluble nitrocellulose	44·0
Insoluble nitrocellulose	30·4
Metallic nitrates	14·0
Vaseline	6·0
Camphor	4·0
Moisture	1·6

Earlier varieties employed resin, the vaseline or camphor being omitted. E.C. powder is of historical interest, as being the first smokeless powder.

Ecrasite. An Austrian military high explosive consisting of the ammonium salt of trinitro-cresol.

Fulminate of silver AgONC. The silver salt of fulminic acid. It is made in a similar manner to mercuric fulminate. It is, however, much more sensitive. Its use is confined to toy fireworks, crackers, etc., which are not allowed to contain more than a very limited amount.

Fulminating silver. Ag_3N, is the nitride of silver. It is made by treating the oxide with ammonia. It is too sensitive and unstable for general use as an explosive.

Gelatine dynamite consists of about 70 per cent. nitroglycerine plus collodion cotton, potassium nitrate, and wood meal. Calcium carbonate or mineral jelly is used as a stabilizer.

Gelignite is very similar to gelatine dynamite, but contains a reduced proportion (60 per cent.) of nitroglycerine. Other varieties embody sodium or barium nitrate in place of some or all of the potassium nitrate. To permit of its use at low temperatures, dinitro-toluene, T.N.T. or dinitro-glycol are introduced. These substances have the effect of depressing the freezing-point of the nitroglycerine.

Hexanite. (hexanitrodiphenylamine). An explosive having properties generally similar to those of picric acid. Mixtures of hexanite and trotyl were used in Germany for filling bombs and torpedoes.

Hexanitro-ethane $C_2(NO_2)_6$. A neutral crystalline solid melting at 142° C. It is soluble in most organic solvents, but only slightly in cold alcohol. It is insoluble in water. To blows or friction it is very insensitive, but it can be detonated. Alone, or with oxidizing agents, it forms a powerful high explosive. It is, however, too unstable for general use.

Melinite. A French high explosive. There are different types. All contain picric acid, but other constituents such as cresylite are found. Paraffin wax is added to decrease the sensitivity.

Mercurit. A German blasting explosive. It consists of 88 per cent. potassium chlorate, and 12 per cent. neutral tar oil of high boiling-point. Another variety embodies potassium perchlorate in place of some of the chlorate.

Nitrolit. A high explosive used for shell fittings by the Germans. It consists of ammonium nitrate and tri-nitro-anisol.

Oxyliquit. A blasting explosive consisting of liquid oxygen, absorbed in some porous combustible such as cork or charcoal. It has the advantage of being cheap, and, for blasting purposes, there is little danger attending a missfire, as the explosive becomes inert in a short time owing to the evaporation of the oxygen.

Panclastite (Turpinite). Liquid nitrogen peroxide and carbon bisulphide, nitrobenzene or nitrotoluene are the constituents. It is very powerful and violent, but dangerous to handle owing to the poisonous and volatile nature of the first-named constituent. The two constituents are kept separate until the explosive is required.

Pannonit. An Austrian blasting explosive, having an interesting constitution.

Nitroglycerine	25·5
Collodion cotton	1·5
Ammonium nitrate	37
Dextrin	4
Glycerine	3
Nitro-toluene	5
Sodium or potassium chloride	24

Penthrite (tetranitropentaerythritol or pentaerythritol tetranitrate) is made by nitrating pentaerythritol, which is derived from acetaldehyde and formaldehyde. It can thus be manufactured synthetically from simple raw materials. It is a powerful high explosive somewhat similar to nitroglycerine, but is solid, having a melting-point of 140° C.

Poudre B. The French Service propellant. It consists of nitrocellulose gelatinized with ether-alcohol. Diphenylamine is used as a stabilizer. Various sizes are used, denoted by an initial indicating the purpose for which it is used, *e.g.* " Poudre BF " for rifles (from fusil).

Poudre J. A French smokeless powder for shot-guns and revolvers.

Nitrocellulose	83
Ammonium bichromate	14
Potassium bichromate	3
Moisture	3

Poudre M. Another shot-gun powder much used in France.

Nitrocellulose	71
Barium nitrate	20
Potassium nitrate	5
Camphor	3
Binding material	1

Poudre S is a French shot-gun propellant similar to Poudre M.

Poudre T is a French sporting powder consisting mainly of guncotton gelatinized with acetone, and incorporated with gum and graphite. 2 per cent. of potassium nitrate is added during the early stages of manufacture, but most of this is removed by washing in a later stage.

Prometheus. A French explosive consisting of a porous oxygen carrier and a liquid combustible. The two constituents are kept separate until required for use ; when the former is dipped in the latter.

Oxygen carrier	Potassium chlorate	95	90	80
	Manganese dioxide	5	10	20
Combustible	Nitro-benzene	50	60	
	Turpentine	20	15	
	Naphtha	30	25	

Any of the different oxygen carriers may be mixed with either of the combustibles. The disadvantage of this explosive is the uncertain and irregular results consequent on the varying amounts of liquid taken up by the porous oxygen carrier (from 8 to 13 per cent.).

Pyrocollodion is nitrocellulose containing 12·6 per cent. nitrogen.

Schneiderite. A French high explosive used as a shell filling.

Ammonium nitrate	8·74
Dinitro-naphthalene	12·6

Schultze powder. The first successful smokeless powder. A modern variety has the following constitution :

Insoluble nitrocellulose	55
Soluble nitrocellulose	27
Metallic nitrates	11·2
Vaseline	5
Moisture	1·8

The nitrocellulose is obtained from wood cellulose.

Sprengel explosives. This is the general name given to the type of explosive invented by Dr. Hermann Sprengel, F.R.S., in 1871.

They consist essentially of two components, an oxidizing agent and a combustible, which are segregated until required for use. In this way, all danger of premature explosion is eliminated.

Suitable oxidizing agents that have been suggested or used are :

Nitric acid, potassium chlorate, nitrogen peroxide, etc. As combustibles, the following may be mentioned : nitro-benzene, nitro-naphthalene, carbon bisulphide, petroleum, picric acid, etc.

They are not used in Great Britain as the necessary admixture of the two components is only permissible in a properly licensed explosives factory.

Examples of these explosives mentioned in this dictionary are panclastite and prometheus.

Super-excellite. A widely used coal-mine explosive. The composition of No. 3 is as follows :

Nitroglycerine	9·5
Collodion cotton	0·5
Ammonium nitrate	59·0
Starch	4·5
Castor oil	1·0
Sodium chloride	15·0
Ammonium oxalate	10·5

The use of collodion cotton should be noted.

Turpinite. (*See* **Panclastite.**)

APPENDIX V.

PHYSICAL DATA OF CHEMICALS.

Legend. i. = Insoluble, s. = Soluble
s.d. = Soluble with decomposition
v.s. = Very soluble
s.s. = Sparingly soluble
v.s.s. = Very sparingly soluble
Referring to Solubility in water
dec. = Decomposes
w.c.s. = White Crystalline Solid

Name	Chemical Formula	Melting-point ° C.	Boiling-point ° C.	Appearance	Solubility in water	Chief uses in explosives work
Acetone ...	$(CH_3)_2CO$	−95°	56·5°	Colourless liquid. Creosote odour	v.s.	Solvent
Alcohol ...	$C_2H_5.OH$	−115°	78·5°	Colourless liquid. Vinous odour	v.s.	Solvent
Aluminium	Al	657°	1800°	Silver grey	i.	As powder—for Incendiaries, Ammonals, etc.
Ammonia	NH_3	−75°	−33°	Colourless gas with pungent odour. Fumes with H Cl	v.s. alkaline solution	For ammonium salts
Ammonium Chloride ...	NH_4Cl	dissociates to NH_3 and H Cl at 350°		w.c.s.	s.	Fumyls
Ammonium Perchlorate	NH_4ClO_4	dec. explosively		w.c.s.	s.	Pyrotechnics. Mining Explosives
Antimony Sulphide (Stibnite)	Sb_2S_3	546°	—	Dark grey to black powder	i.	Cap compositions. Pyrotechnics

Name	Chemical Formula	Melting-Point ° C.	Boiling-Point ° C.	Appearance	Solubility in water	Chief uses in explosives work
Arsenic disulphide Redorpiment, realgar	As_2S_2	320°	565°	Red powder	i.	Pyrotechnics
Arsenious Sulphide (Orpiment)	As_2S_3	310°	707°	Yellow Powder	i.	Pyrotechnics
Barium Nitrate	$Ba(NO_3)_2$	575°	dec.	w.c.s.	s.	Baratol Pyrotechnics
Benzene ...	C_6H_6	5·4°	80·2°	Colourless liquid	i.	For Nitrobenzenes
Calcium Carbonate (Chalk)	$CaCO_3$	decomposes at 825°C. to lime and CO_2		White powder	i.	Stabilizer for Nitrocellulose
Carbon Tetrachloride	$C\ Cl_4$	$-23°$	76°	Colourless Violatile liquid with strong smell	i.	Berger Smoke Compositions
Carbamite	$Co[N(C_6H_5)(C_2H_5)]_2$	72·5°	—	White solid with characteristic odour	i.	Stabilizer
Caustic Soda	NaOH	318°	—	White solid	v.s.	For making phenol. As an alkali
Charcoal	C	Sublimes at about 4,000°		Black powder	i.	For gunpowder
Chlorsulphonic Acid	$Cl.SO_3H$	—	about 156°	Fuming Liquid	s.d.	For Smokes
m.Dinitrobenzene	$C_6H_4(NO_2)_2$	91°	302°	Pale yellow crystals	v.s.s.	Constituent of Bellite
Diphenylamine	$(C_6H_5)_2\ NH$	54°	302°	White Solid	i.	Stabilizer
Dinitrophenol	$C_6H_3(OH)(NO_2)_2$	110° to 114°	Explodes	Yellow-Brown Crystals	s.s.	Shellite
Ether ...	$(C_2H_5)_2O$	$-123°$	34·6°	Colourless mobile liquid with ethereal odour	v.s.s.	Solvent

Name	Chemical Formula	Melting-point ° C.	Boiling-point ° C.	Appearance	Solubility in water	Chief uses in explosives work
Fulminate of Mercury	$Hg(ONC)_2$	Ignites	at 160°	White, grey or brown crystals	i.	Detonators. Cap compositions
Glycerol	$C_3H_5(OH)_3$	17°	290° with dec.	Colourless, viscid liquid with sweet taste	v.s.	For making Nitroglycerine
Hammer Scale (Magnetic Oxide of iron)	Fe_3O_4	1538°	—	Heavy black powder	i.	Thermite
Hexachlorethane. (Perchlorethane)	C_2Cl_6	Straight to vapour at 185°		w.c.s.	i.	Berger Smoke Compositions
Kieselguhr	Mainly Silica SiO_2	Softens 1200° Melts 1500°	— — —	Porous white solid (Skeletons of diatomacae)	i.	As absorbent for Nitroglycerine in Dynamites
Lead azide (lead nitride)	PbN_6	Explodes at 320° to 390°		White or buff crystals	i.	Detonators
Lead Styphnate	$C_6H(NO_2)_3O_2Pb, H_2O$	Ignites at 255°		Yellow crystals	i.	Detonators
Linseed Oil (Boiled)	—	—	—	Thick yellow-brown oil. " Hardens " in air	i.	Stabilizer to prevent corrosion of metallic ingredients in pyrotechnic compositions
Magnesium	Mg.	633°	1120°	Silver grey; metallic	i.; but slowly corroded	Pyrotechnics
Milk Sugar (Lactose)	$C_{12}H_{22}O_{11}H_2O$	203° with decomposition		w.c.s.	s.	Pyrotechnics
Nitric Acid	HNO_3	−41·3°	86°	Colourless liquid when pure. Usually brown due to NO_2	v.s.	Nitrating Acid

Name	Chemical Formula	Melting-Point ° C.	Boiling-Point ° C.	Apearance	Solubility in water	Chief uses in explosives work
Nitrocelluloses	Various. Up to 13·7 per cent. Nitrogen	Explodes		White fibrous solid	i.	Cordites. Guncotton for demolitions
Nitroglycerine	$C_3H_5(ONO_2)_3$	13°	Explodes	Colourless oil	v.s.s. (1 in 800)	Cordites, Dynamites, Gelignites, etc.
Paraffin Wax	C_nH_{2n+2} where n is about 28	About 60°	—	Colourless waxy solid	i.	Stabilizer, especially in Pyrotechnics
Phenol	C_6H_5OH	42·7°	181·5°	w.c.s.; turns pink in air and light	v.s.s.	For Picric Acid and Dinitrophenol
Phosphorus, Red	P_4	Changes to white variety on heating		Chocolate red Powder	i.	Match Compositions
Phosphorus. White		44°	287°	Pale yellow solid	i.	Smokes
Picric Acid (Lyddite)	$C_6H_2(NO_2)_3OH$	121·6°	Explodes	Intense yellow crystals	s.s.	Used alone for H.E., and in shellite
Potassium Chlorate	$KClO_3$	357°	dec. at 400°	w.c.s.	s.	Pyrotechnics. Mining Explosives
Potassium Nitrate (Nitre)	KNO_3	337°	dec. at 400°	w.c.s.	s.	Gunpowder
Potassium Perchlorate	$KClO_4$	about 610° with decomposition	—	w.c.s.	s.s.	Pyrotechnics. Mining Explosives
Silicon Tetrachloride	$SiCl_4$	−89°	57·5°	Fuming Liquid	s.d.	Smokes
Sodium Hydroxide	(*See* Caustic Soda)					
Sodium Carbonate (Soda Ash)	Na_2CO_3	852°	dec.	White powder	s.	In Pyrotechnics to give yellow flame
Stannic Chloride (Tin Tetrachloride)	$SnCl_4$	−33°	114°	Fuming Liquid	s.d.	Smokes

Name	Chemical Formula	Melting-Point ° C.	Boiling-Point ° C.	Appearance	Solubility in water	Chief uses in explosives work
Strontium Carbonate	$SrCO_3$	decomposes at at 1340°		white powder	i.	To colour flames red
Strontium Nitrate	$Sr(NO_3)_2$	decomposes at at 645° C.		w.c.s.	s.	Oxidizing agent. For red flares
Sulphur ...	S_8	113° (rhombic)	444·5°	Yellow crystalline solid	i.	Gunpowder. Pyrotechnics
Sulphuric Acid	H_2SO_4	10·5°	dec. 400°	Heavy colourless oil	v.s. much heat	In Nitrating Acid
Tetrachlorethane	$C_2H_2Cl_4$	−44°	146°	Colourless liquid	i.	Berger Smoke Compositions
Titanium Tetrachloride	$TiCl_4$	−25°	136°	Fuming liquid	s.d.	Smokes
Tetryl (C.E.)	$C_6H_2(NO_2)_3N(CH_3)NO_2$	129°	Explodes	Pale yellow crystals	i.	Exploders
Toluene ...	$C_6H_5.CH_3$	−94°	110°	Colourless liquid	i.	For T.N.T.
Trinitrotoluene Trotyl T.N.T.	$C_6H_2(NO_2)_3CH_3$	80·5°	Explodes	Pale yellow crystals	i.	As Burster. In Amatol and Baratol
Zinc Dust	$Zn+ZnO$	For Zinc: 418°	918°	Grey powder	i.	Berger Smoke Compositions

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