Amended by amendment passed by W.O. dated 18th March 1927.
" " " " " " " " 30th March 1928.

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TEXT BOOK OF EXPLOSIVES

USED IN THE SERVICE

1925

By Command of the Army Council,

H J Creedy

THE WAR OFFICE,
   18th February, 1925.

ERRATA.

PICTORIAL REPRESENTATIONS OF CORDITE.

SHEET 1.

1

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1.
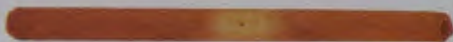2. } NEWLY MADE CORDITE.
3. } SHOWING RANGE IN COLOUR.
4.

5. EARLY STAGE OF CORROSION OF CORDITE MD SIZE 16.

PICTORIAL REPRESENTATIONS OF CORDITE.

SHEET 2

6

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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.

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.

Chapters I to XIV (inclusive) are based on lectures delivered to
the Advanced Class at the Artillery College, Woolwich.

The large (kilogram) Calorie is used for purposes of illustration
throughout the book. Physical constants are, as far as possible,
drawn from Kaye and Laby's Tables of Physical Constants, 1921.

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

Flow Diagrams are used freely ; these summarise 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.

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.

Figures in parenthesis in the text, or at the end of a paragraph, are
references to Appendix I.

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.

INTRODUCTORY.

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 fundamental features possessed by an explosive are thus :—

(i) Potential energy in virtue 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.

By the choice of explosive chemical compounds, by mixing them in suitable proportions, and by the modification of their physical form, 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 centimetres per second, or it may be caused to rise to velocities of the order of 8,000 metres per 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 internal combustion engines.

2. Liquid.

As in the case of nitroglycerine.

3. Solid.

As in the case of picric acid or tri-nitro-toluene.

Some explosives used in the service are of a horny and flexible consistency (*e.g.*, cordites); but more generally, in their final form, service explosives are rigid solids. In general too, efforts are made to obtain them in as dense a condition 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 second, may become as great as 300 tons per 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.

Ammonium carbonate can be decomposed into products which are entirely gaseous :—

$$(NH_4)_2 \ CO_3 \rightleftharpoons 2NH_3 + CO_2 + H_2O$$
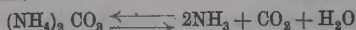
But this entails an absorption of heat, and no explosion takes place.

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 :—

$$3 \ Fe_3O_4 + 4Al_2 \longrightarrow 4Al_2 \ O_3 + 9Fe$$
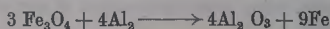
There is no evolution of gas, and so no explosion, but the mixture, which is known as "thermit," has been used commercially for welding, and in the Service for incendiary purposes. Temperatures of 2500° C. can thus be obtained in a closed mould. All metals, with the exception of tungsten, *tantalum and molybdenum* are melted before this temperature is reached.

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

$$2C_3H_5 \ (NO_3)_3 \longrightarrow 6CO_2 + 5H_2O + 3N_2 + O$$

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 nitroglycerine 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.

The gases most frequently liberated in an explosion are carbon monoxide, carbon dioxide, nitrogen and water vapour.

The formation of chemical compounds from their elements is usually accompanied either by an absorption or by a liberation of

heat, known as the *heat of formation*. Compounds are termed *endo-thermic* 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, an amount of heat is given out equal to the heat of formation of the compound.

Explosives such as nitroglycerine and picric acid break down on explosion with the formation of the exothermic compounds carbon monoxide, carbon dioxide and water vapour, with the liberation of their respective heats of formation. Thus :—

$$2C + O_2 \longrightarrow 2CO + 29.2/·/ \text{ Cals. per grm. mol.} carbon \ as \ diamond \ (A).$$

$$C + O_2 \longrightarrow CO_2 + 9\overset{+}{7}·3. \text{ Cals. per grm. mol.} carbon \ as \ diamond. \ (B).$$

$$2H_2 + O_2 \longrightarrow 2H_2O + \begin{matrix} 58·1. \text{ If retained as vapour.} \\ 69·0. \text{ If condensed as liquid.} \end{matrix} \left.\begin{matrix} \\ \end{matrix}\right\} \begin{matrix} \text{Cals per} \\ \text{grm. mol.} \end{matrix} \ (C).$$
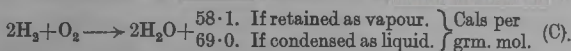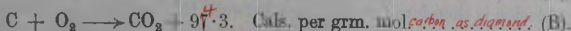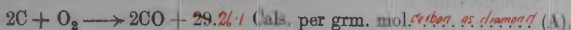
From (C) it will be seen that more heat energy is liberated if the water vapour is condensed, but from an explosive point of view, this is not available in practice. (A) and (B) show that an extra 68·3 Calories of heat per gram molecule are liberated when the carbon is completely oxidised to dioxide, as against the partial oxidation to monoxide. This represents extra energy, and can only be obtained if the oxygen content of the explosive, like that of nitroglycerine, is sufficiently high. As will be seen when the classification of explosives is con-sidered, an explosive compound having a deficit of oxygen content may be mixed with another containing surplus oxygen in order to produce a mixture " balanced " in this respect. This ensures the entire oxidation of the carbon to dioxide, which not only secures the maximum liberation of heat energy, but may also be of secondary importance when it is essential that the products of explosion should be non-poisonous.

Very few individual compounds are thus " balanced." Dinitro-glycol is, however, an example. It is a very powerful explosive, and is said to have been largely manufactured in Germany during the Great War. It decomposes thus :—

$$\begin{matrix} H_2CONO_2 \\ | \\ H_2CONO_2 \end{matrix} \longrightarrow 2H_2O + 2CO_2 + N_2$$
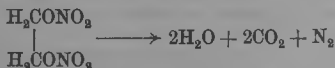
When a compound breaks down on explosion, the heat generated is the sum of the heat of formation of the compound (whether positive or negative), and of the heats of formation of the products of explosion.

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

$$PbN_6 \longrightarrow Pb + 3N_2 + 105·9 \text{ Calories per gram molecule.}$$

Mercuric fulminate which contains oxygen is another example of

an endothermic compound. Its decomposition may be represented as follows :—

$$Hg\,(OCN)_2 \longrightarrow Hg + 2CO + N_2 + 110 \text{ Calories per gram molecule.}$$
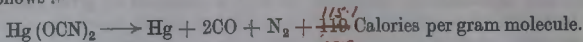
The total heat evolved is the sum of 61 Calories per gram molecule given out by the breakdown of the fulminate, together with the further heat liberated by the formation of the exothermic carbon monoxide. The latter has previously been shown to be 29 Calories per gram molecule, and since 2 molecules are formed in this reaction, the heat of decomposition of the fulminate is augmented by a further 58 Calories per gram molecule.

Nitroglycerine is an exothermic compound which gives out 98·9 Calories per gram molecule in its formation. The heat produced on explosion is therefore the difference between this quantity and the sum of the heats of formation of the various products. The decomposition proceeds thus :—

$$2C_3H_5(NO_3)_3 \longrightarrow 6CO_2 + 5H_2O + 3N_2 + O + 676·5 \text{ Calories.}$$
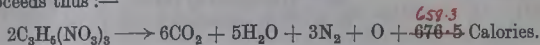
The total heat liberated may be shown as follows :—

Heat of formation of CO_2 + heat of formation of H_2O — heat of formation of nitroglycerine.

$$6(97·3) + 5(58·1) - 2(98·9)$$
$$= 583·8 + 290·5 - 197·8$$
$$676·5 \text{ Calories for 2 gram molecules,}$$
$$\text{or } 338·2 \text{ Calories per gram molecule.}$$

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 the former get oxygen from the air, the latter 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, or employed for disruptive and destructive operations, whether industrial or military.

CHAPTER II.

CLASSIFICATION OF EXPLOSIVES.

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 two 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, and 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 by Orders in Council, as the necessity arises. (1)

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 Appendix V, Magazine Regulations. Explosives in Groups V to XIII— except those specially stored as in paras. 120 and 121—must, and those in Groups III and IV may, be stored in an explosives store ").

Section II of Magazine Regulations defines " magazine conditions " in detail.

Division into groups is based on the following principles :—

Stable explosives, bearing explosion risk, and demanding magazine precautions in storage and handling to obviate spark or friction ; and

explosives liable to decomposition bearing an explosion risk, must be stored in a magazine.

Explosives liable to decomposition bearing technically a fire risk ; and stable explosives bearing fire or explosion risk (not included in Group I) may be stored in a magazine *or* an explosives store.

The explosives not included in the above 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, nitrocellulose powders, etc., etc.).

2. *High Explosives.*

       (i) Bursting charges (lyddite, trotyl, amatols, etc.).

      (ii) Intermediaries (picric powder, composition exploding, etc.).

     (iii) Initiators (mercuric fulminate, lead azide, etc.).

     (iv) Demolition and mining charges (guncotton, etc.).

3. *Miscellaneous.*

       (i) Smoke producers.

      (ii) Light producers.

     (iii) Day signals.

     (iv) Incendiary compositions, etc.

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 over-strain the gun. Propellant charges of cordite or other explosive are made up from sticks, tubes, or slabs of the explosive substance ; and the shape and 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 the rapid erosion of the bore of the gun, 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, and, 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 explosives, but which, on account of their nature, need similar precautions for their safe handling and storage. Their uses are sufficiently indicated by their names.

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 oxidises 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, fall under this heading. It has been seen (Chap. I) that the products of explosion depend upon 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

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of oxygen. In this case the unoxidised carbon is set free, resulting in characteristic black smoke.

$$C_7H_5\,(NO_2)_3 \longrightarrow 7CO + 5H_2O + 3N_2 + 7C.$$
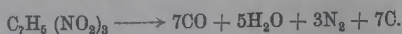
Some inorganic compounds (*e.g.*, chlorates, perchlorates, ammonium nitrate, etc.) may also be classed under this heading.

(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 upon 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 Chap. I.

2. *Explosive mixtures.*

This class may also be conveniently considered under two headings :—

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

Cordites	}	(Containing both nitrocellulose and nitro-
Ballistite		glycerine.)
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 oxidised. 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 mixtures 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. (2)

The velocity of the explosion wave in a gaseous mixture of oxygen and hydrogen 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 per second.

3. Transition   ..   A period of rapid increase of velocity to that of detonation.

4. Detonation   ..   At a uniform velocity of several thousand metres per second.

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.

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With initiators and intermediaries the first three periods are very short. Shell fillings, 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
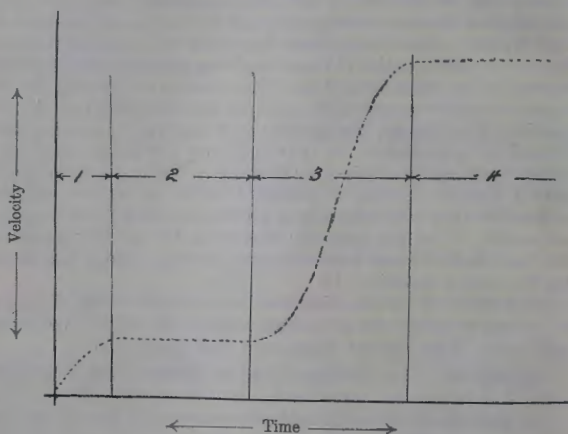
Fig. 2.1 (not drawn to scale).

Velocity-Time curve of an explosive wave in a gaseous mixture of Oxygen and Hydrogen.

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.

Burning is the comparatively slow oxidation (accompanied by the evolution of heat and light) of a combustible body by the oxygen of the air.

Internal burning is the name given to combustion in which the substance burning contains its own supporters of combustion. It is quite distinct from burning in air, and independent of any substance outside the explosive itself.

Explosion is a rapid combustion. Its velocity may vary from about $\frac{1}{3}$ of a metre per second (if controlled, as with modern propellants), up to about 300 metres per second (under the severest conditions as to pressure, etc.). It is, however, fairly constant for a given substance, provided the latter is homogeneous, and under constant conditions of pressure and temperature.

Detonation is a molecular splitting up, followed, in the case of oxygen bearing compounds, by a practically instantaneous burning. It proceeds in a wave throughout the substance. The maximum velocity of the wave is very quickly reached, and then remains constant for a given explosive at a given density. Velocities of detonation may vary from about the order of 3,000 metres per second, up to the order of 8,000 metres per second, according to the nature of the explosive and its physical condition.

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 in 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, though explosives similar in constitution to the amatols had been in commercial use for many years prior to 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 realised, 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, though 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 as recently as 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, though many accidents both in this country and abroad, acted as deterrents to their manufacture on a commercial scale.

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 two main types are :—

				Cordite Mark I. Per cent.	Cordite M.D. Per cent.
Guncotton	..	..	..	37	65
Nitroglycerine	..	..	..	58	30
Mineral jelly	..	..	..	5	5

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.

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, though 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.

Trinitro-phenyl-methyl-nitramine 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 of 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.

From the foregoing brief review, it is 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 seaborne. 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 (3).

Ammonia can be catalytically oxidised 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, $30 \cdot 2$ per cent. came from Chile saltpetre, $26 \cdot 6$ per cent. from ammonia recovery from the distillation of coal, and $43 \cdot 2$ per cent. from synthetic methods (4).

The following figures (5) give some idea of the tremendous output of the most important high explosives during the 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 only 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 upon 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 hydro carbon 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 XV.

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 a 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.

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

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

Gunpowder gives 193.
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 due 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 were 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 stabiliser. 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 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 :—*

    In order to be safe for transport ; and to withstand the shock of discharge, when used as a shell filling.

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

    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 XV.

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.

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 under certain conditions reacts somewhat readily with some metals, freeing mercury and becoming inert from an explosive point of view. Mercury thus set free may cause minute intercrystalline cracks in the metal of the containing vessel. " Season cracking " in brass has been traced to this cause.

(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 propellent, 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, though not necessarily, contains mercuric fulminate. The cap may be enclosed in a tube, fuze or cartridge case, etc., according to the purpose 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 presented 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 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 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 that 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, though 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 unit mass of 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 upon 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 upon 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.

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 apparatus for determining pressures. This measures the " time-integral " of a pressure wave set up by a detonation, over a definite short period of time (of the order of 1/200,000th second). The momentum produced in a given mass in the period of time is measured, and from this, the pressure producing it can be approximately computed.

The apparatus is represented diagrammatically in Fig. 4.1. A definite quantity of the detonating explosive (B) is placed in position under certain standard conditions, and detonated by means of an initiator (A), usually discharged by a swinging weight (W). A " degrading pellet " (C) of asbestos and magnesia is placed between the explosive and the bar itself (D) to prevent damage to the latter. This is a circular bar of steel, suspended in convenient supports. At its further end is a second small bar (E) of the same material and cross-section, called the " time-piece." The contiguous surfaces of the two bars (D) and (E) are carefully worked and polished, so that they fit together with the greatest nicety and are easily made to adhere by means of a slight film of vaseline. Just beyond the " time-piece " is a small ballistic pendulum (F), whose function is to catch the " time-piece " when it is thrown forward, as explained later, and to measure

its momentum by recording the swing of the pendulum on a smoked-glass surface (H) by means of a stylus (G). The pendulum is hung by threads so that it can only oscillate in one plane, and is box-shaped for the reception of the " time-piece."

The detonation of the explosive (B) initiates a compression wave which passes along the bar (D) from left to right. This wave travels with the velocity of sound in steel (about 17,000 feet per second), passes on to the " time-piece " (E), and is reflected back from its free right-hand surface as a tension wave. It may be noticed that there are no air gaps in the system ; detonator, " degrading pellet," pressure bar, and " time-piece " are in successive contact with each other. When the amplitude of the tension wave exceeds that of the compression wave at the surface junction of (D) and (E), the surfaces will separate, the momentum trapped in the " time-piece " (E) (which will now be propelled to the right, falling into, and giving up its momentum to the pendulum (F)) being the " time-integral " of the pressure wave over the period it takes to travel to and fro through the length of the " time-piece " (E). The length of the latter thus determines the period over which the pressure of detonation will be measured, i.e. the time
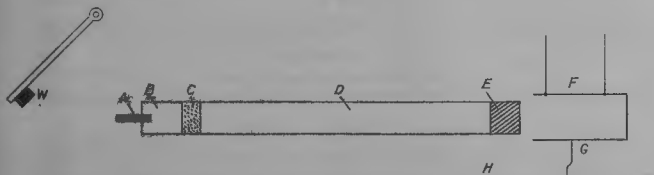
FIG. 4.1.—Diagrammatic representation of the Hopkinson Pressure Bar.

it takes a sound wave to travel twice the length of the " time-piece " (forwards, and back again after reflection).

In the actual apparatus the various parts are so dimensioned that the pressure in tons per square inch exerted by the detonation of the explosive, works out to be an exact multiple of the length of the record scratched on the smoked glass. A single linear measurement and simple multiplication thus give the required pressure, from any one experiment.

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 the above-mentioned " degrading pellet," which is scattered on explosion, is interposed between the explosive and the end of the bar. It is made of standardised 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

(B 28–231)z   C

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 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 for typical propellants are given below. (6)

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	933	961
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°	4056°	3488°

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

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 does not alter the latter velocity. (7)

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 that 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.
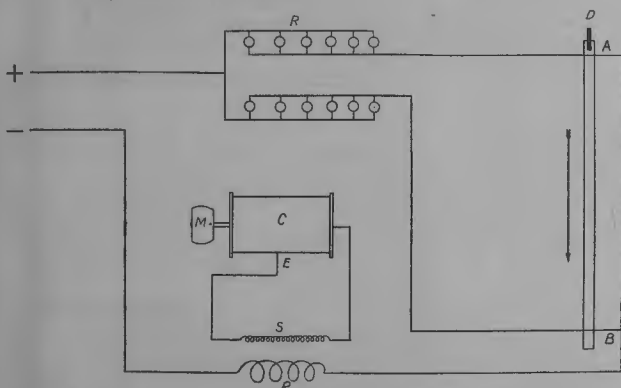
FIG. 5.1.—Diagrammatic representation of the Mettegang Recorder.

(a) *The Mettegang Recorder.*

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

Velocities of detonation are given in the chapters on different explosives, and will be found tabulated in Appendix II.
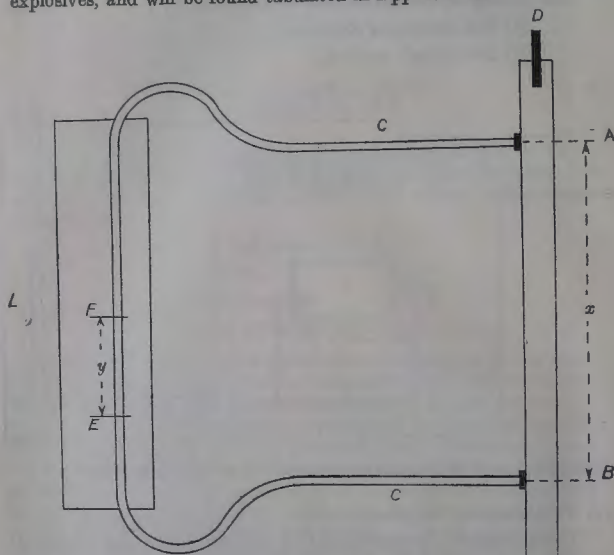
FIG. 5.2.—Dautriche's method for the determination of velocities of detonation.

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

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

It is of interest to note that a detonating impulse will travel through metals of high elasticity, and through water. Though 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 which 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 under 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.

A definite blow is applied to a thin layer of a certain quantity of the explosive on a steel anvil, by means of a weight falling in guides from a measured height. The height necessary to cause 50 per cent. of explosions is found experimentally. The ratio of this height to the corresponding height required to explode picric acid under similar conditions is multiplied by 100, and given as the figure of insensitiveness of the explosive. The higher this figure, the safer is the explosive against direct impact. The actual apparatus is designed to admit of the measurement of the volume of gas evolved from the explosion, and from this the effect of the impact is judged.

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 box-wood 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
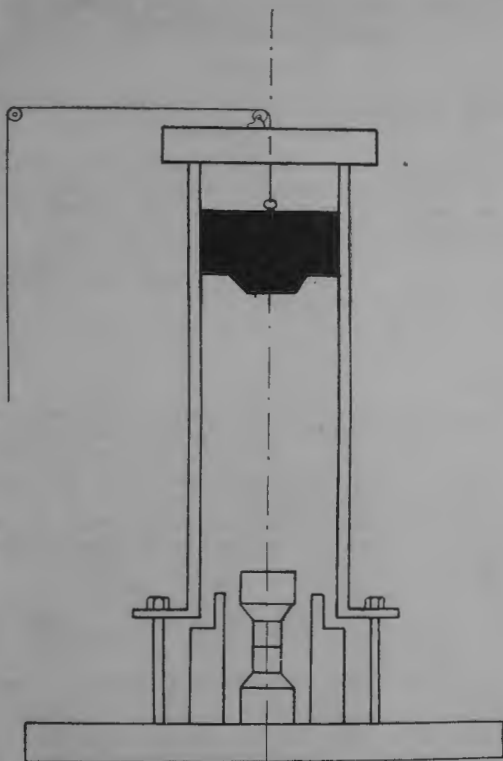
Fig. 5.3.—Diagrammatic Sketch of Falling Weight Apparatus.

others, such as nitrogen iodide, are too sensitive to stand even ordinary handling without explosion.

" Figures of insensitiveness " will be found in Appendix II.

C.—MANUFACTURE OF HIGH EXPLOSIVES AND THE SUBSTANCES ENTERING INTO THEIR COMPOSITION.

CHAPTER VI.

PICRIC ACID, DINITROPHENOL, LYDDITE, SHELLITE, PICRIC POWDER.

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 TRINITROPHENOL.
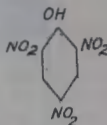
Introduction.

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.   Mononitrophenol.   m-Dinitrophenol.   Symmetrical Trinitrophenol.
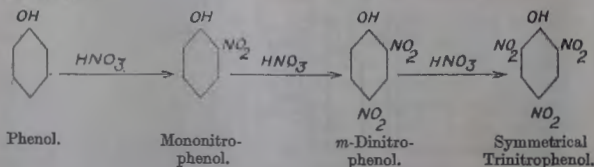
Trinitrophenol cannot be made satisfactorily by the direct action of nitric acid on phenol.

(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.   Phenol m-disulphonic acid.   Picric Acid.
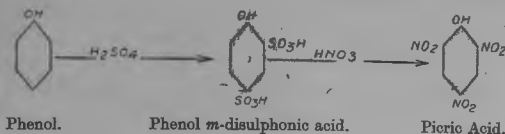
(ii) From chlorbenzene. This process is important, as it furnishes a means of obtaining dinitrophenol which is itself important as a constituent of high explosives.

Chlor- m-Dinitro-   Sodium m-dinitro- m-Dinitro-   Picric
benzene.   chlorbenzene.   phenolate.   phenol.   acid.
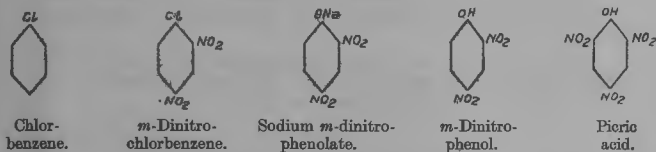
Picric acid is deficient in oxygen, with the result that on detonation, free carbon is liberated, causing the familiar black burst of a lyddite shell.

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. In France (with collodion), it is known as melinite; in Japan, as shimose powder; and in Germany as Granatfüllung C/88.

Raw Materials and their Manufacture.

1. *Phenol.*

Phenol is the starting point in the majority of the processes for manufacturing picric acid.

When pure, it is a white crystalline solid, having a melting point of 42·5° C. and a boiling point of 182° C. It is more usual to find crystals of a deep rose tint due to slight oxidation.

It is an acid, as its common name, carbolic acid, indicates.

Before the Great War, all the phenol required for the manufacture of explosives in this country was obtained from the distillation of coal tar. This source of supply was found to be totally inadequate when it came to meeting war-time demands, and "synthetic" methods of obtaining phenol were adopted to augment the supply. The manufacture of "synthetic" phenol was well established on the continent prior to 1914, but had not been developed in this country.

2. *Phenol from Benzene through Benzene-sulphonic Acid.*

This was the chief method by which "synthetic" phenol was made in this country. Described briefly, the process consists of the sulphonation of benzene to benzene-sulphonic acid; this is fuzed with caustic soda giving sodium phenolate, from which phenol is obtained by acidification with sulphuric acid.

| Benzene. | Benzene sulphonic Acid. | Sodium Phenolate. | Phenol. |

3. *Chlorbenzene.*

This compound is a derivative of benzene. It is readily made by passing chlorine into benzene until chlorination to monochlorbenzene has taken place.

Dichlorbenzene is also formed at the same time, but is easily separated from monochlorbenzene by fractional distillation; the former boils at 172° C., and the latter at 132° C.

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.

FLOW DIAGRAM FOR MANUFACTURE
OF PICRIC ACID.

Phenol

12 hrs. at 80°C
Steam heating | *Sulphonator* | ⟵ H_2SO_4

Phenol Sulphonic Acid

*Dilution with waste liquid
from previous operations
cooling and settling*

| *Nitrater* | ⟵ $HNO_3(65\%)$

Crude Picric Acid   *Crystallises out on cooling*

Spent Acid ⟵ | *Drainer* |

Spent Acid ⟵ | *Crusher* |

Waste Acid ⟵ | *Counter Current
Washing* | ⟵ *Water*

Water ⟵ | *Centrifuge* |

Picric Acid + 5% Moisture

| *Drying Stoves* |

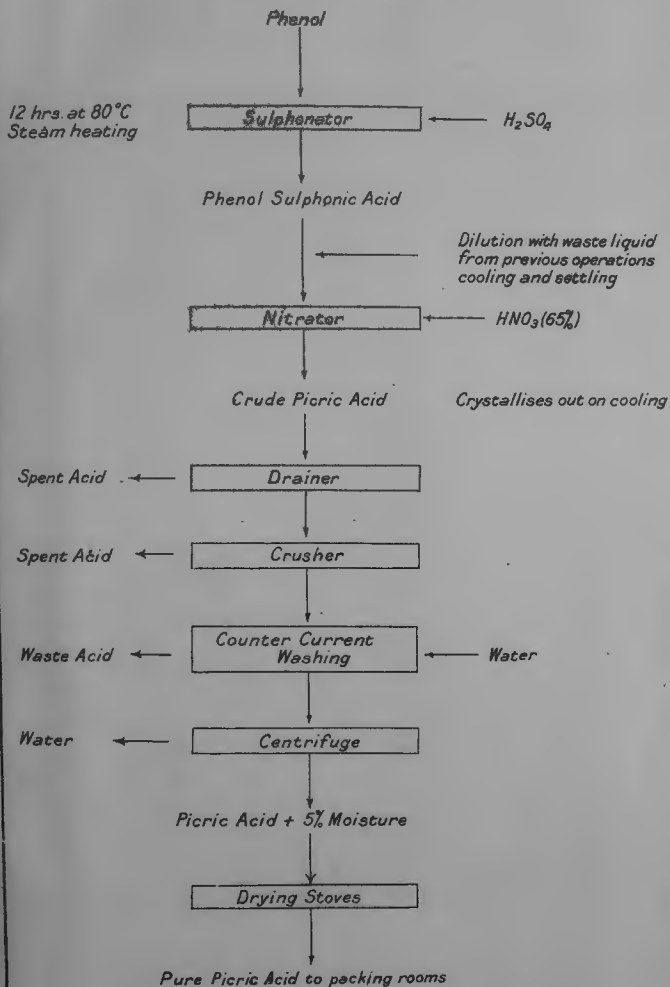*Pure Picric Acid to packing rooms*

FIG. 6.1.

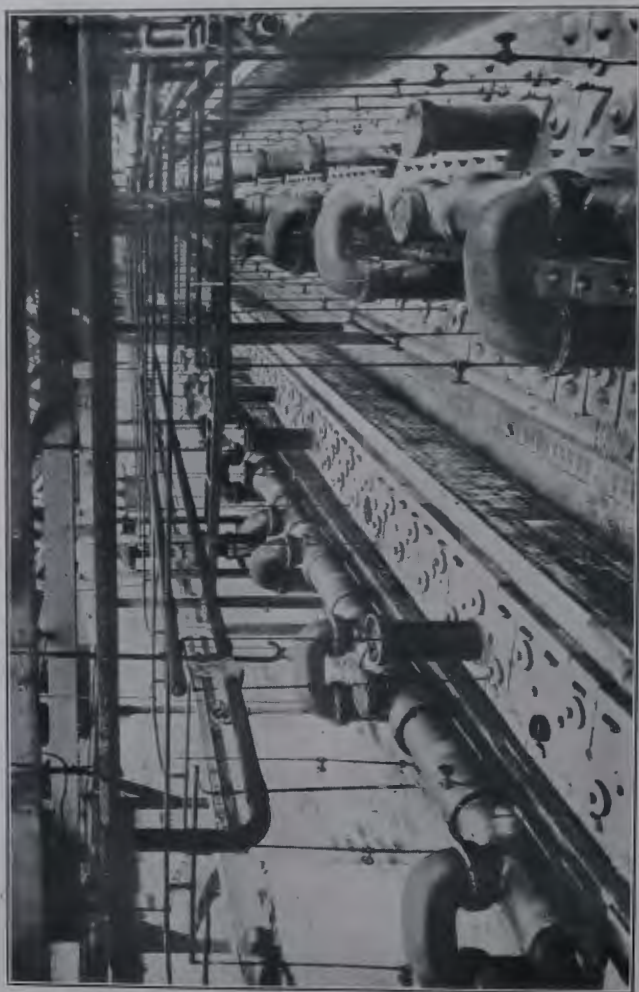FIG. 6.2.—Picric Acid Manufacture.   Pot Process.

Fig. 6.3.—Picric Acid Manufacture.   Continuous Process.

2. Nitration.

The phenol disulphonic acid is weighed out into charges corresponding to about 35 lbs. 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 absorption 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 crystallises 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. 6.1 ; a nitrating house being shown in Fig. 6.2.

(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. 6.3.

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 crystallises 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 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 poisonous to the skin.

(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 recrystallisation, 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 acid 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 chanbers, 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.

Of the impurities in picric acid, the picrates of lead and calcium are the chief. The former can be avoided by using lead-free materials ; the latter is introduced in the washing water, which may contain lime in solution.

Oxalic acid and oxalates are also found. The metallic picrates are undesirable as they are highly sensitive, and are therefore a source of danger.

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. These salts are usually 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).

Picrate.						*Figure of Insensitiveness.*
Copper	..	..	..	..	..	~~10~~ 89
Lead	..	..	..	..	..	18
Silver	..	..	..	..	..	74
Sodium	..	..	..	..	..	92
Zinc	..	..	..	..	..	107
Ammonium		..	..	..	..	120

Lead picrate is particularly sensitive, and therefore great importance must be paid to the absence of lead from all paints, metals and materials with which picric acid is likely to come in contact, either in its manufacture or use.

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. It may be of interest, however, to note the underlying reasons for these tests.

(i) The Melting Point Test.

This detects the presence of dinitrophenol, which lowers the melting point.

(ii) Volatile Matter.

The percentage of volatile matter is an indication of the amount of 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.

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*.

CHAPTER VII.

TROTYL, NITROGEN FIXATION, AMMONIUM NITRATE, AMATOL, DINITROTOLUENE, AMATOXOL.

(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 as recently as 1863 by Wilbrand, and 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.

Toluene.　　M.N.T.　　D.N.T.　　T.N.T.
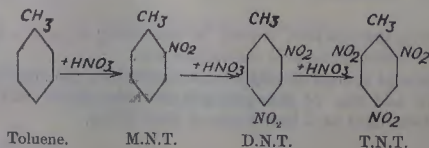
The above gives an approximate representation of the nitration of toluene, which is given more fully in Fig. 7.1. It will be noticed that there is only one *symmetrical* trinitrotoluene; the other trinitro-bodies, of which there are five in all, are known as the *unsymmetrical* T.N.T.'s.

On detonation T.N.T. is converted into a mixture of gases. The following figures, from Bichel, give the approximate composition of

NITRATION OF TOLUENE.
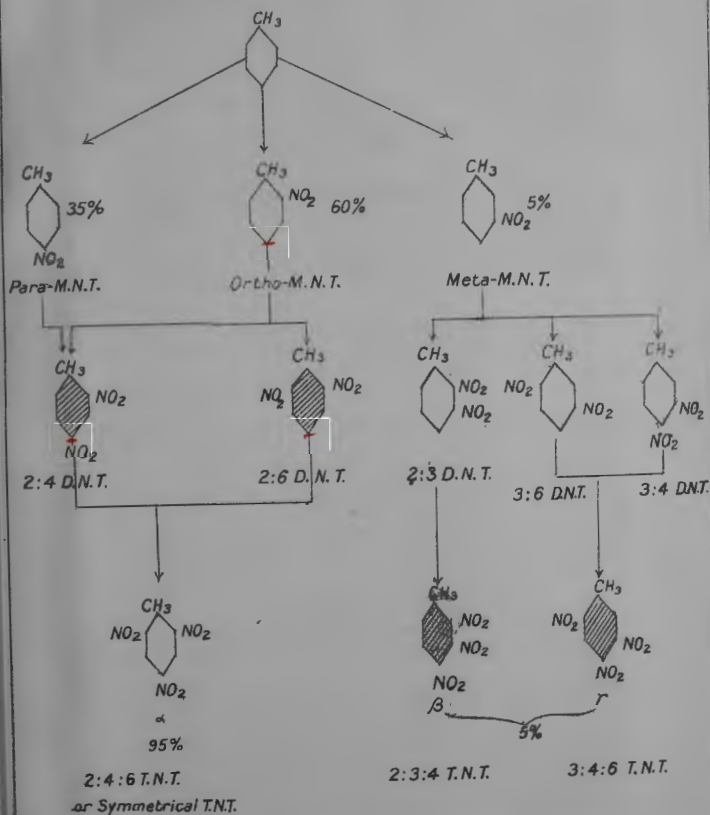
The Isomers which cause exudation are shaded.

FIG.7.1.

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	..	..	..	..	..	6·2 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.

Raw Materials and their Manufacture.

Toluene.

This hydrocarbon is derived from two main sources : (1), from the products of distillation of coal ; and (2), from the distillation of petroleum found in Borneo.

1. When coal is distilled toluene is recovered in two ways ; (i) from the gas by scrubbing, and (ii) by fractional distillation of the coal tar. An appreciable amount of toluene was obtained from this source during the war.

2. Ninety-five per cent. of the toluene used for T.N.T. manufacture during the war came from Borneo petroleum. This petroleum is particularly rich in the aromatic hydrocarbons, of which toluene is an important member. By partial distillation before shipment the proportion of toluene in the exported product was raised to about 50 per cent. The distillate, known as " toluene-petrol " or " toluene-benzine " was then shipped to this country in tank vessels.

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 $\frac{1}{4}$ 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.
              { 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 (2a). 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 problem of *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.

FLOW DIAGRAM FOR QUEENSFERRY PROCESS.
(T.N.T)

"Toluene-Petrol"

MNT SECTION

Waste Acid to ← NITRATOR ← Mixed Acid 62% { 21% H_2SO_4
Denitrators   62% HNO_3
                          MNT Petrol   21% { 17% H_2O

Petrol ← STILL

MNT

NITRATION HOUSE.

Waste Acid to ← SUPER-DETOLULATOR
Denitrators

        Acid   Twice used Acid
        MNT
        DETOLULATOR

Once used   DNT
Acid   TRINITRATOR ← Trinitrating { 78% H_2SO_4
                              Mixed Acid { 18% HNO_3
                                          { 4% H_2O

        TNT & Acids

        SEPARATOR

        Acid TNT

Washings ← WASHER ← Hot Water

        TNT

Washings ← PELLETER ← Cold Water

        "Pellite"

PURIFICATION HOUSE

Washings ← MELTER ← Steam and Hot Water

        Molten TNT

        CRYSTALLISER ← Solution of Na_2SO_3 (a)

Waste   TNT Crystals
Liquor
        FILTER → To Waste.

        TNT Crystals

To Waste ← WASHER ← Steam and Hot Water (b)

        Wet TNT

To Waste ← DRIER ← Steam and Warm Water

        Molten TNT

Warm Water ← FLAKER ← Cold Water

        Flake TNT

(a) Converts β & γ TNT into soluble products.
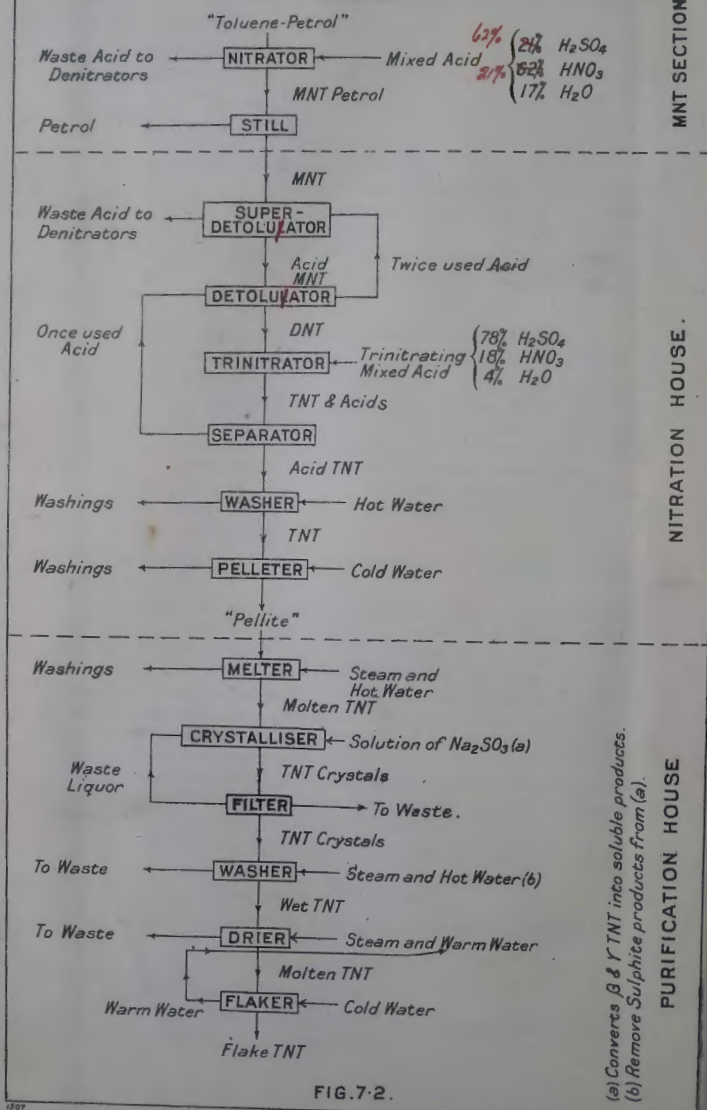(b) Remove Sulphite products from (a).

FIG. 7·2.

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, to form a compound which almost instantaneously decomposes. 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. (*see* page 56) and the use of weak basic 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. 7.1, the remainder being unimportant. The two unsymmetrical T.N.T's. shown, are known as β and γ T.N.T., which melt at 112° C. and 104° C. respectively. The elimination of these 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 sensitive, and is therefore a source of danger.

(ii) If the exploder system is not contained in a steel container, the exudation products may saturate the substances in the system and render it inert. For this reason C.E. is always used instead of trotyl for exploder systems for use in the tropics, and steel exploder containers are preferable for shell filled with a T.N.T. explosive.

Two methods of eliminating the unsymmetrical T.N.T's. 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 (*see* page 44). Interaction between the sulphite and the unsymmetrical isomers 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-crystallisation of the T.N.T. from a hot alcohol solution will give a purer product ; washing with cold alcohol is also efficacious.

2. A reference to Fig. 7.1 will show that the unsymmetrical T.N.T·s. 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. 7.2 gives a flow diagram of this process. It is divided into three parts.

1. *The M.N.T. Section.*

(i) The " toluene-benzine," as received from overseas, is nitrated, using a mixed acid consisting of 81 per cent. sulphuric acid, 62 per cent. nitric acid and 17 per cent. water. This converts the toluene into M.N.T., while the remainder of the " toluene-benzine," 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. 7.3.)

(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 (page 52).

(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

ROCESS.

M.N.T.

Water

from M.N.T. Storage

Superdetoluator
Coils not shewn

from Mixed Acid

Storage

Air

Mixed Acid Egg
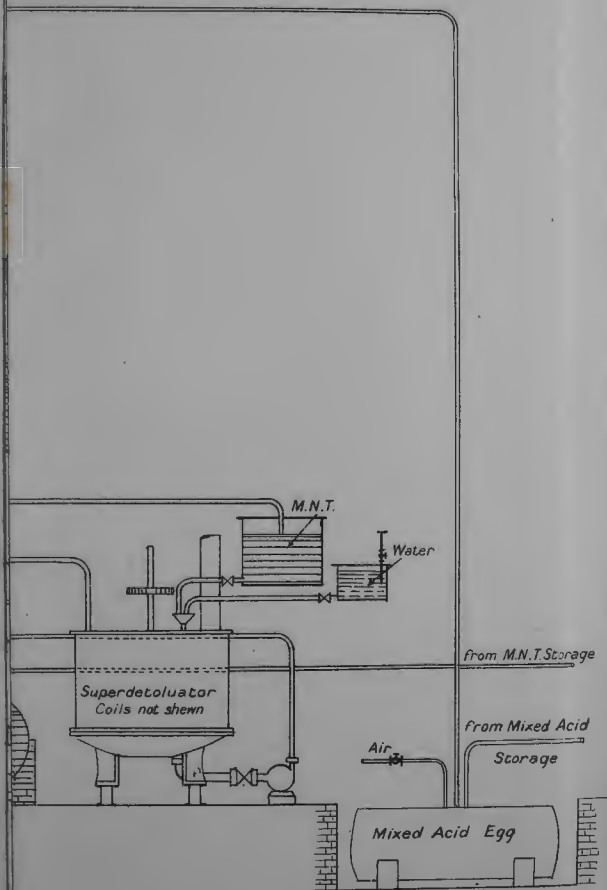
cent. nitric acid, and 4 per cent. water. A section through a nitrator is given in Fig. 7.4.
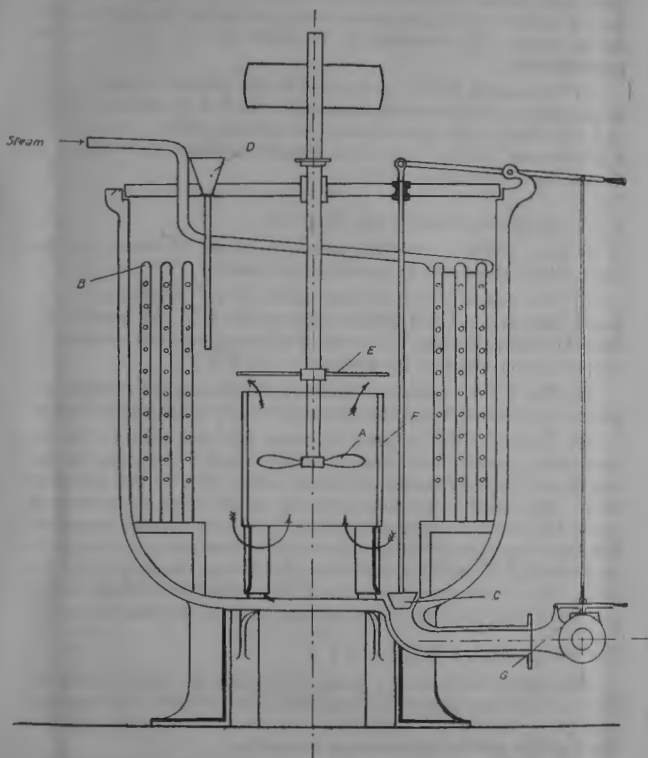
FIG. 7.4.

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 propellor) 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.

(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.

(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. 7.5.)

(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 " crystalliser " 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 3 nitrators and 3 settlers, arranged in pairs and connected together, as shown in Fig. 7.6.

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

HEWING

ed Tank.

Steam.

To Fan.

Drier. Two of
these in series.

Cooler.

Granulating
Roll.

eam.

Water from Granulator Roll.

er supply.

Water Supply.

Packing.

Malby & Sons, Lith
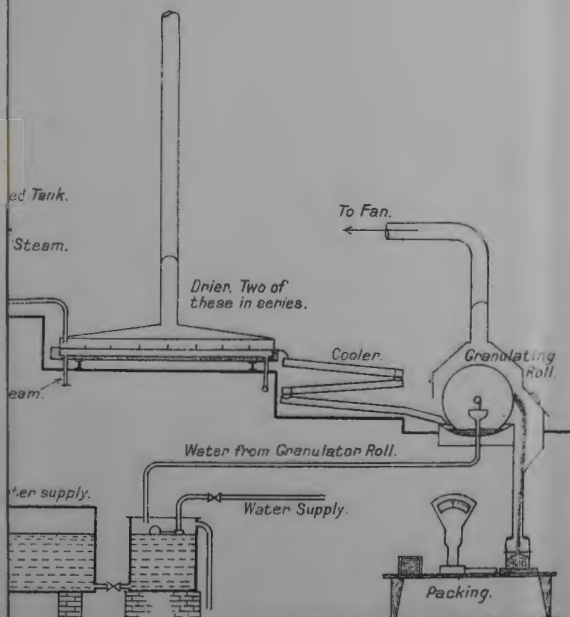
next nitrator, and the acids travel in the opposite direction. Thus the nitration is carried out by acid that is progressively stronger as the nitration approaches completion.

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.
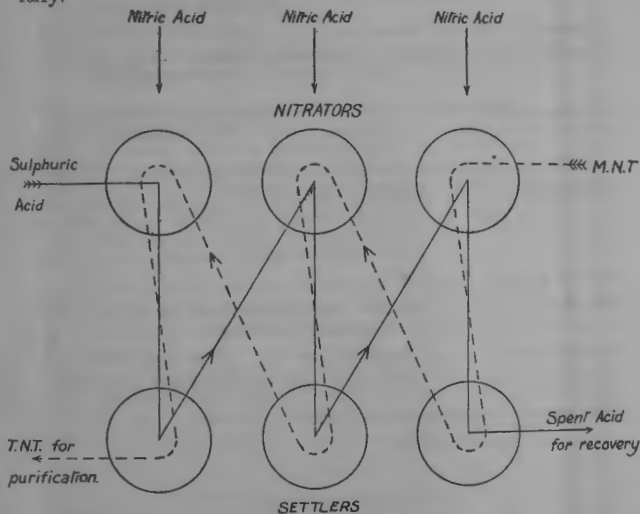
FIG. 7.6.—Diagram of the Oldbury Continuous Process for the nitration of Toluene to T.N.T.

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 washhouses), thorough ventilation, use of milk, 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 very insensitive to shock and friction; operations such as milling and crushing can be carried out in perfect safety.

58

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	...	Practically non-reactive.	Reactive with alkalies to form sensitive 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 ...		$81 \cdot 5°$ 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	..	$80°$ C.
Stability	..	Good. Decomposition is very slow at $140°$ C. Practically non-reactive.
Insensitiveness	..	Impact figure 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 $79 \cdot 5°$ C.
Less pure than Grade 1.
Other properties are similar to Grade 1.
Used in the amatols, etc.

TROTYL (GRADE 3).

Melting point. $76°$ C.
Stability. Almost as good as Grade 1.
Insensitiveness. A little more sensitive than Grade 1.
Slightly less powerful than pure trotyl, and more poisonous.

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.
This grade is practically obsolete for military purposes.

The tests applied to T.N.T. for acceptance and grading are five in number.

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 unnitrated substances.

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 soluble in acetone and 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. to form a compound which afterwards breaks down into this "transformation product." The amount present is only small, but it is extremely undesirable. It is very sensitive to heat, shock or friction, and, due to further decomposition, there may be a risk of spontaneous ignition, though this awaits definite proof. 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.

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 give more powerful results, but are a great economy as ammonium nitrate is cheap in comparison with T.N.T.

NITROGEN FIXATION AND AMMONIA. (9).

Nitrogen in the form of nitrates and ammonia, may be called the keystone of the explosives industry, and a ready access to an abundant supply is an asset of the first order in time of war.

There are three main sources of fixed nitrogen :—

   (i) The nitrate beds in Chile.
   (ii) By-product recovery in the distillation of coal.
   (iii) The atmosphere.

(i) *The Nitrate beds of Chile.*

The crude sodium nitrate is shipped to this country and purified by recrystallisation. The manufacture of nitric acid from this salt is discussed in any book on Inorganic Chemistry (8). The great disadvantage of this source is the necessity for overseas transport, which is vulnerable in war-time. In addition, modern demands on these nitrate beds must lead to their early exhaustion.

The next two sources have the advantage of being indigenous to this country.

(ii) *By-product recovery in the distillation of Coal.*

When coal is subjected to destructive distillation in a coke oven or gas retort, gas, tar and a watery liquor are produced. The gas on leaving the retort is cooled, and much of the nitrogen that was originally present in the coal is recovered, as ammonia, from the watery liquor referred to above, and from the condensed liquor from the coolers. The liquor is boiled with milk of lime, which liberates the ammonia as a gas.

The gaseous ammonia is absorbed in sulphuric acid and crude ammonium sulphate separates. To purify it, the crude ammonium sulphate is digested with milk of lime, and the pure ammonia which is so liberated is again absorbed in sulphuric acid.

Ammonium sulphate is prepared in large quantities in peace time for use as an artificial fertiliser, and it is therefore readily available for the manufacture of ammonium nitrate by one, or other, of the methods to be described later.

(iii) *The Atmosphere.*

The fixation of atmospheric nitrogen has been a chemical problem of immense difficulty, and its satisfactory solution is an event of comparatively recent years. The three most important methods which have been commercially successful are : (*a*) The " Haber " process ; (*b*) the " Cyanamide " process ; and (*c*) the " Arc " process.

(*a*) *The Haber Process.*

This is a method of making synthetic ammonia by the direct combination of nitrogen and hydrogen.

$$\tfrac{1}{2}N_2 + 3H_2 \rightleftharpoons \tfrac{1}{2}NH_3$$
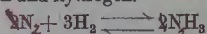
The reaction is reversible, and a reasonable yield of ammonia can only be obtained in the presence of a catalyst under correct conditions of pressure and temperature.

Nitrogen and hydrogen are introduced into the vessel in which the reaction takes place, in approximately molecular proportions. The maximum yield of ammonia is obtained when the pressure exceeds 100 atmospheres and the temperature is about 500° C.

The nitrogen is conveniently prepared from liquid air by fractional distillation.

The hydrogen can be obtained from water gas, which is made by passing steam over red hot coke. Water gas consists almost entirely of hydrogen and carbon monoxide (CO) in approximately equal proportions. If an excess of steam be mixed with the water gas and the mixture be passed over specially prepared iron or copper (which acts as a catalyst) at a temperature of rather less than 500° C., the carbon monoxide is oxidised to the dioxide (CO_2) at the expense of the steam, with the liberation of a further amount of hydrogen.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The hydrogen is readily separated from the mixture of hydrogen and carbon dioxide by absorbing the latter in water under pressure.

The power required for this process is ·43 kilowatt-years per ton of nitrogen fixed.

(b) The " Cyanamide " Process.

When calcium carbide (CaC_2) (8) is heated to 1000° C. in an atmosphere of nitrogen, it combines with it to form calcium cyanamide ($CaCN_2$).

$$CaC_2 + 2N \longrightarrow CaCN_2 + C.$$

The calcium cyanamide can be converted to ammonia and calcium carbonate by treatment with superheated steam at a pressure of 50 to 250 lbs. per square inch.

$$CaCN_2 + 3H_2O \longrightarrow 2NH_3 + CaCO_3$$
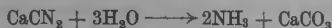
This process was patented in 1895. It is fairly economical in power, requiring 2·2 kilowatt-years per ton of nitrogen fixed.

(c) The " Arc " Process.

When air is heated to a very high temperature such as that which exists in the vicinity of an electric arc, the nitrogen and oxygen present combine to form nitric oxide (NO). On cooling, the nitric oxide takes up more oxygen from the atmosphere to form nitrogen peroxide (NO_2). This can be absorbed in water to form nitric acid.

This process is very wasteful of energy, using 8·56 kilowatt-years per ton of nitrogen fixed, and therefore its development has been mostly confined to places where water power is cheap and abundant.

Oxidation of Ammonia to form Nitric Acid.

As the processes (iii), (*a*) and (*b*) above, yield nitrogen in the form of ammonia, some direct method of converting this ammonia to nitric acid is desirable.

In 1839 a process was discovered by Kuhlmann, a Frenchman. and developed since 1900 by Professor Ostwald. If ammonia and oxygen are passed rapidly over a surface of platinum gauze (or other suitable catalyst) at a temperature of 300° C., about 85 per cent. of the ammonia is oxidised to water and nitric oxide.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

The nitric oxide combines with more oxygen to form nitrogen peroxide (NO_2) which is absorbed in water to form nitric acid.

$$4NO + 3O_2 + 2H_2O \longrightarrow 4HNO_3$$
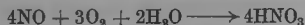
This process was extensively used in Germany during the war, and formed her main source of supply.

Experimental work has been done on other processes ; for example, the Bucher " Cyanide " process, in which sodium cyanide is formed by the interaction of nitrogen, carbon and sodium carbonate in the presence of an iron catalyst.

AMMONIUM NITRATE. NH_4NO_3.

Ammonium nitrate is usually obtained from ammonium sulphate in a manner to be described. It was formerly made by direct neutralisation of nitric acid by ammonia.

Manufacture of Ammonium Nitrate. (Freeth Process).

$$2NaNO_3 + (NH_4)_2SO_4 \longrightarrow 2NH_4NO_3 + Na_2SO_4.$$
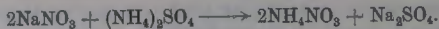
This equation represents the reaction.

It will be noticed that all the salts involved are soluble in water, and therefore it is a matter of some difficulty to arrange the strengths of the solutions in such a manner that one of the salts may be precipitated.

The principle employed in the manufacture of ammonium nitrate by this method may be stated thus : A solution of ammonium nitrate, sodium sulphate and sodium nitrate, existing at a temperature of not less than 60° C. and not in contact with any of these salts in their solid state, may be so diluted that on cooling to a pre-determined temperature, the sodium salts will remain in solution and the ammonium nitrate will crystallise out.

The process is cyclical and will be quite clearly illustrated if one cycle is considered.

1. Consider the stage in the cycle at which the ammonium nitrate has been crystallised out. To the mother liquor is added the liquor from the washing of the sodium sulphate precipitate (*see* 4 below) and any other wash liquor.

2. The mixed liquors are concentrated to an extent sufficient to remove an amount of water equivalent to that added in the previous cycle.

3. Equivalent quantities of ammonium sulphate and sodium nitrate are added to the concentrated liquor, the total addition being equivalent to the amount of ammonium nitrate removed in the previous cycle. The reaction between the two salts results in the precipitation of an amount of sodium sulphate equivalent to the amount of ammonium sulphate and sodium nitrate added. The temperature throughout this stage and the next is maintained at 70°–90° C.

4. The sodium sulphate is filtered off, and after separation of the filtrate, is washed ; the wash liquors going back to stage 1. The filtrate, *without* any added wash water, is diluted with sufficient water to keep the impurities in solution, and cooled to the temperature for which dilution has been arranged (usually about 25° C.).

5. Ammonium nitrate crystallises out, and is drained, centrifuged, and packed. The mother liquor goes back to stage 1 and the cycle is recommenced.

Fig. 7.7 is a flow diagram of the process.

Ammonium nitrate as packed for transport contains about 3 per cent. of moisture. If the moisture content is reduced to a lower figure, water is absorbed from the air. This results in the ammonium nitrate caking together into a hard mass which is very difficult to crush into the fine form in which it is used.

Properties of Ammonium Nitrate.

Ammonium nitrate is a colourless crystalline salt, melting at 170° C. when quite pure and dry. It exists in several different crystalline forms ; changes taking place from one form to another at

FREETH PROCESS FOR MAKING AMMONIUM NITRATE.

NaNO₃
(NH₄)₂SO₄

Water

Mixing Tank.

Stirrer.

Washings.

Na₂SO₄ (solid)   Water.

Water

Rotary Filter.   Na₂SO₄

NH₄NO₃ + a little NaNO₃   Re-washing Tank.

Dilution Tank.

Crystalliser

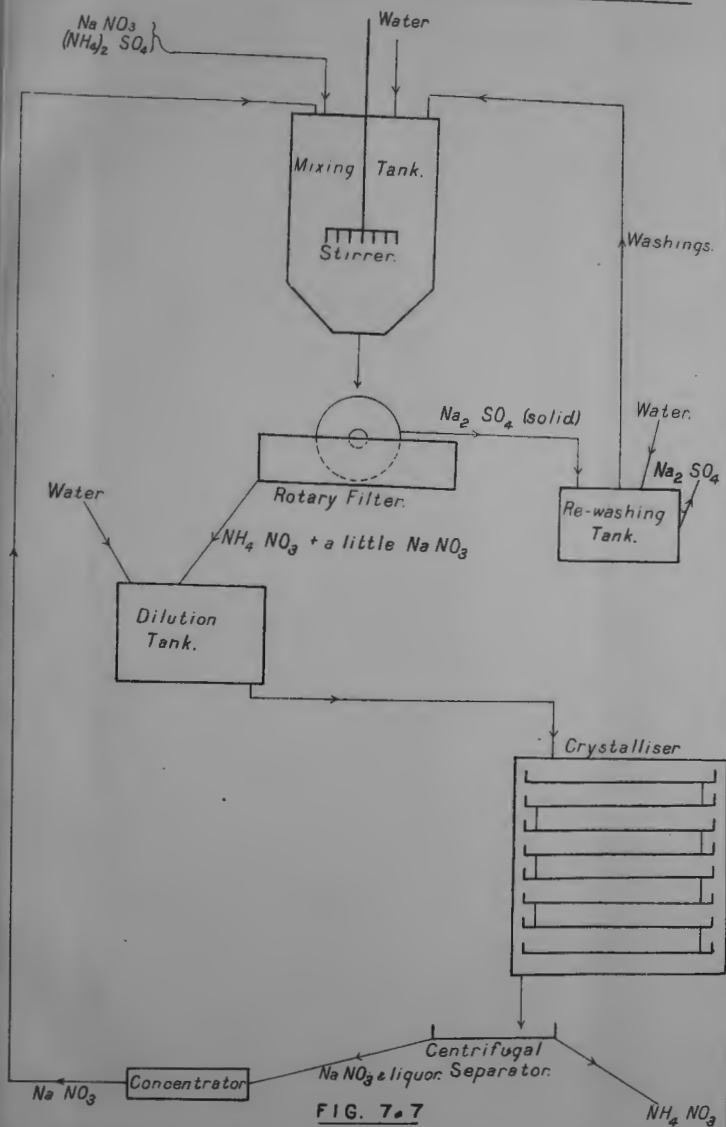Na NO₃   Concentrator   NaNO₃ & liquor.   Centrifugal Separator.   NH₄NO₃

FIG. 7.7

perfectly definite temperatures. One of these changes occurs at
32° C., which is of especial importance in the filling of shell with
amatol. This change is accompanied by an increase in density, and
the consequent shrinkage may introduce an air gap into the detonating
system, and, breaking its continuity, tends to render it ineffective.

Ammonium nitrate reacts with most common metals. The
action with aluminium is practically negligible. With iron and lead,
it forms insensitive salts that are harmless from the point of view of
explosives. It forms salts with copper and tin that are somewhat
sensitive, but a still more sensitive compound is formed when tin
and copper are present together as in bronze. This was a cause of
accidents in the early days of amatol manufacture, when, following
on the practice of the gunpowder factories, bronze tools were used.

Ammonium nitrate is graded by analysis into three grades, 1,
2 and 3. The chief impurities are :—

> (i) Moisture.
>
> (ii) Saline impurities.
>
> (iii) Pyridine.
>
> (iv) Thiocyanates.
>
> (v) Acidity.

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

> (a) When 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 coal distillation. 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 set back on discharge, with a consequent danger of
blinds ; in the latter case exudation follows. The gases formed, set up
a pressure which forces out the liquid exudation products, particularly
with 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 shell are not carefully cleaned, remain on the out-
side of the shell or in screw threads and invite prematures. For this
reason particular care has to be taken to ensure that amatol for use in
hot climates is made from the purest ammonium nitrate and trotyl.

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.* In

practice, Grade 2 Trotyl is used with Grade 1 Ammonium nitrate for use in other than tropical stations (when both the ingredients must be Grade 1).

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.

AMATOL.

Amatol is an intimate mixture of ammonium nitrate and trotyl. It was proposed with the object of economising 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 principal amatols are 40/60 and 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 summarised in Table 7.A.

AMATOL 40/60.

General Properties.

Melting point	..	About 76° C.
Stability	..	Satisfactory if the ingredients are pure. If the ammonium nitrate contains sodium nitrate, interaction may set in with the impurities in the T.N.T., but only at very high temperatures (110° to 120° C.).
Insensitiveness	..	Impact figure 120 if pure T.N.T. Impact figure 111 if impure T.N.T. (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. for a 45/55 mixture.
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.

TABLE 7.A.

METHODS OF MANUFACTURE OF AMATOLS.

Composition.		Method of Mixing.	Method of Filling.	Appearance of Burst.	Remarks.
80/20	(a)	Milling in an edge-runner mill.	Stemming. Cavity formed by press-plunger.	Contains sufficient oxygen for complete combustion. (Theoretical quantities 83/17) and therefore practically no smoke.	Porous and therefore liable to absorb moisture before filling.
	(b)	Hot-mixing in a steam jacketed pan.*	Stemmed or extruded : While hot it is in a pasty condition.	A smoke mixture provided to assist observation.	Non-porous and therefore is NOT liable to absorb moisture.
40/60...		Hot-mixing*	When hot, is fluid, and therefore poured.	Deficient in oxygen, and gives smoke on burst.	These two amatols are are very easy to mix and fill and are therefore important in case of emergency.
50/50...		Hot-mixing*	Poured	—	

* Hot-mixing is carried out at about 103° C.

AMATOL 80/20.

General Properties.

Melting point	..	Not readily fusible, but begins to soften at the melting point of crude T.N.T. (76° C.). Advantage is taken of this in the " semi-melt " method of filling.
Stability	..	Good with pure ingredients.
Insensitiveness	..	Impact figure over 120 if pure T.N.T. is used ; 111 if T.N.T. is impure (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 stemming the cold amatol in by mechanical plungers, or, in the " semi-melt " process, the hot plastic mass is compressed into the shell mechanically.

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, though amatol 40/60 may be used in emergency as a large output can be obtained more rapidly by its use.

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 :—

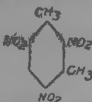|					
Trotyl Grade 2	..	..	..	..	45
Ammonium chloride		..	..	..	40
Ammonium nitrate		..	..	..	15

BARATOL.

This explosive, which is mentioned in Chap. IX (page 78) has recently (May, 1923) become more important. Ammonium nitrate attacks copper to form sensitive salts—barium nitrate does not possess this disadvantage, and baratol has therefore been adopted as the standard filling for grenades and bombs, in which the detonators are contained in copper sheaths.

The fact that baratol is non-hygroscopic is an additional advantage, particularly for grenades and bombs.

Amatoxol.

This is a modified form of amatol 80/20, using "toxol," instead of T.N.T.

Toxol consists of 70 parts of T.N.T. and 30 parts of T.N.X. or

trinitroxylene . Its properties are practically the same

as those of amatol made from crude T.N.T., and on this account must only be employed in temperate climates.

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, the formula of which is quoted above, 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.

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 (*see* Chapter XII), 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 VIII.

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 :—
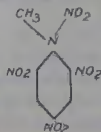
Its stability is lowered by picric acid, and for this reason it is not used as an exploder in lyddite shell; it is unaffected by exudation from T.N.T., but is readily decomposed by alkalies. It contains more nitro-groups, and so a higher oxygen content than either picric acid, or T.N.T., and probably 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 neutralised 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
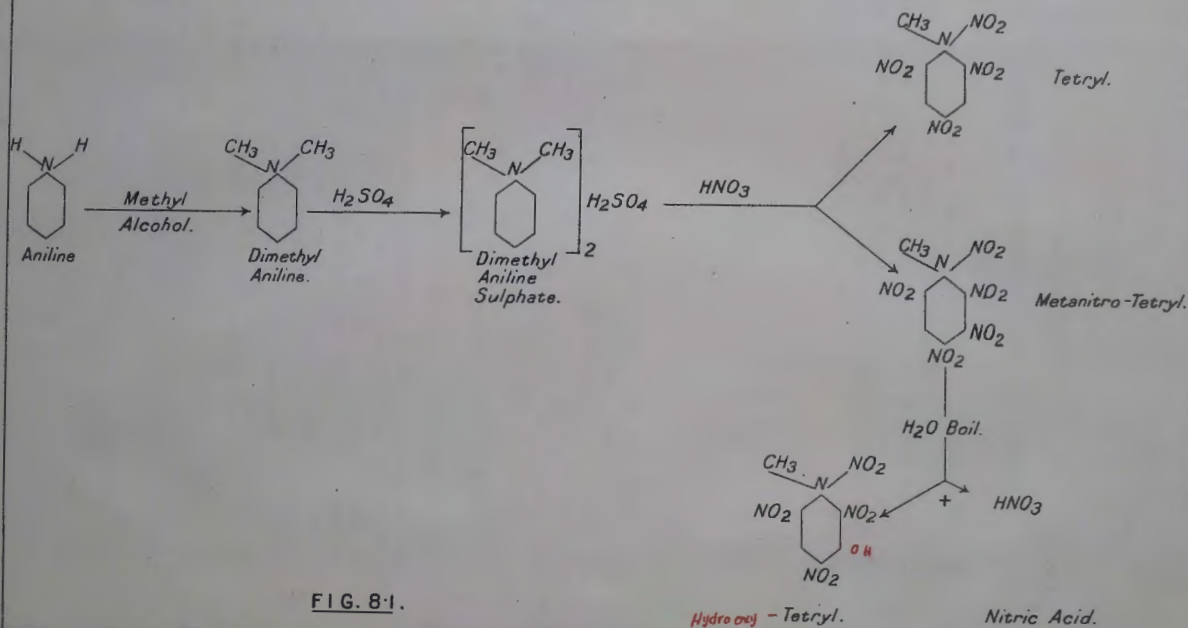
DERIVATION OF TETRYL FROM ANILINE.

FIG. 8·1.

Malby&Sons.Lith.

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 hydrolysed to tetryl and nitric 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.

> (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 summarised as in Fig. 8.1.

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 H.M. Factory at Queensferry.

16 parts of 94 per cent. sulphuric acid, and 6 parts of 90 per cent. nitric acid are used to sulphate and nitrate 1 part by weight of dimethyl aniline. It is found that a large excess of acid minimises 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.

(b) *Nitration.*

This takes place in enamelled iron pots with enamelled stirrers, the pots being jacketed both for steam heating and water cooling. Each pot has a capacity of about 100 gallons, and can deal with a 50 lbs. charge of dimethyl aniline. The charge of nitric acid in the pot is steam heated to about 45° C., and the cooling apparatus then put into operation in the place of the steam heating. The dimethyl aniline sulphate solution is run in, the temperature being allowed to rise at the rate of about 2° C. per minute, until it reaches 70° C. By varying

the inlet flow the contents are kept at this temperature. Care is necessary to prevent the charge catching fire. As this would certainly happen were the stirring to cease, an auxiliary power supply is usually provided to drive the stirring gear in case of a breakdown, or, alternatively, this is accomplished by air injection. For safety, nitrators are separated by brick walls, and each one has a drowning injector fitted to operate through a hole in the fume hood. After nitration the contents are cooled to about 30° C. and run on to the filters. Nitration occupies about 2 hours.

(c) *Filtration.*

Filters are of a type in which the liquid is sucked through the filtering medium by means of a vacuum ; they are run with a vacuum equivalent to 5 to 10 inches of mercury. Graded quartz is the filtering medium. The charge is allowed to stand on the filter for about half an hour before the vacuum is applied ; during this time the greater part of the crude tetryl rises to the surface. It is then drained, but still contains some 50 per cent. of acid. This is removed by subsequent drowning, but no water must enter the filter, for the ensuing heat of dilution of the acid would probably fire the whole charge.

(d) *Drowning and Washing.*

The crude tetryl from the filters is gradually added to water in 100-gallon stoneware vessels, 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 hydrolyses the tetra-nitro-phenyl-methyl-nitramine.

(f) *Centrifuging.*

Washing is continued for some minutes in the centrifuge ; the tetryl is then centrifuged down to about 5 per cent. moisture content. It is now ready for purification.

The manufacturing processes are summarised in a flow diagram in Fig. 8.2.

The spent acid from the filters is run into settling vats, and allowed to stand as long as possible ; fine particles of tetryl which rise to the surface are skimmed off, and returned to the filters. The acid is then treated at 260° C. in shallow cast-iron stills worked on the continuous system. Organic matter is broken up, and nitric acid recovered.

The yield of crude tetryl is 70 to 80 per cent. of that indicated by theory ; the loss is due to the formation of tetra-nitro-phenyl-methyl-nitramine, to oxidation, and to the fact that tetryl is to some extent soluble in the spent acid.
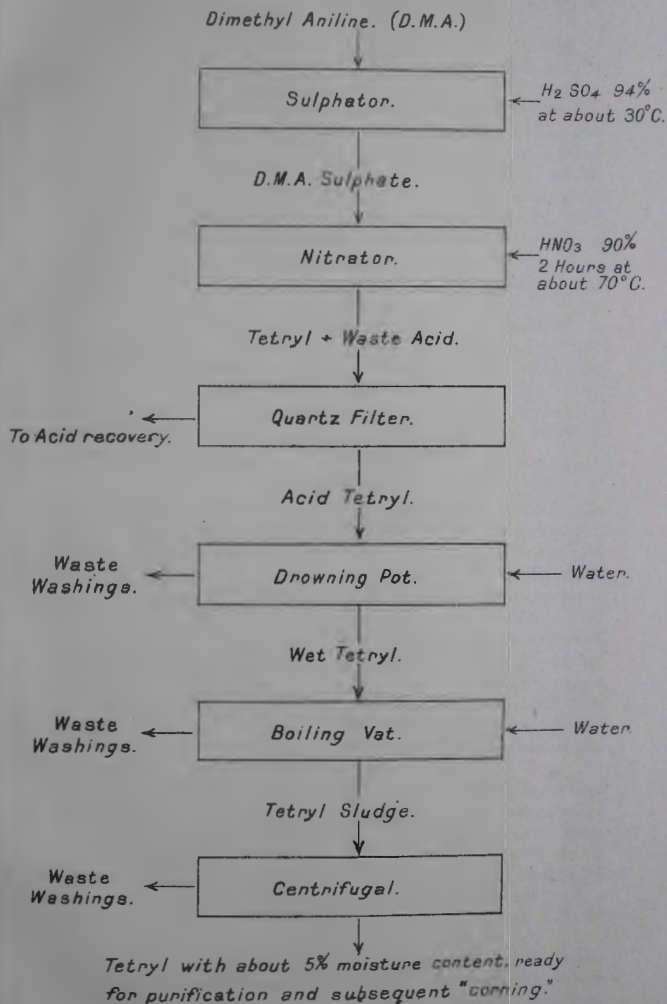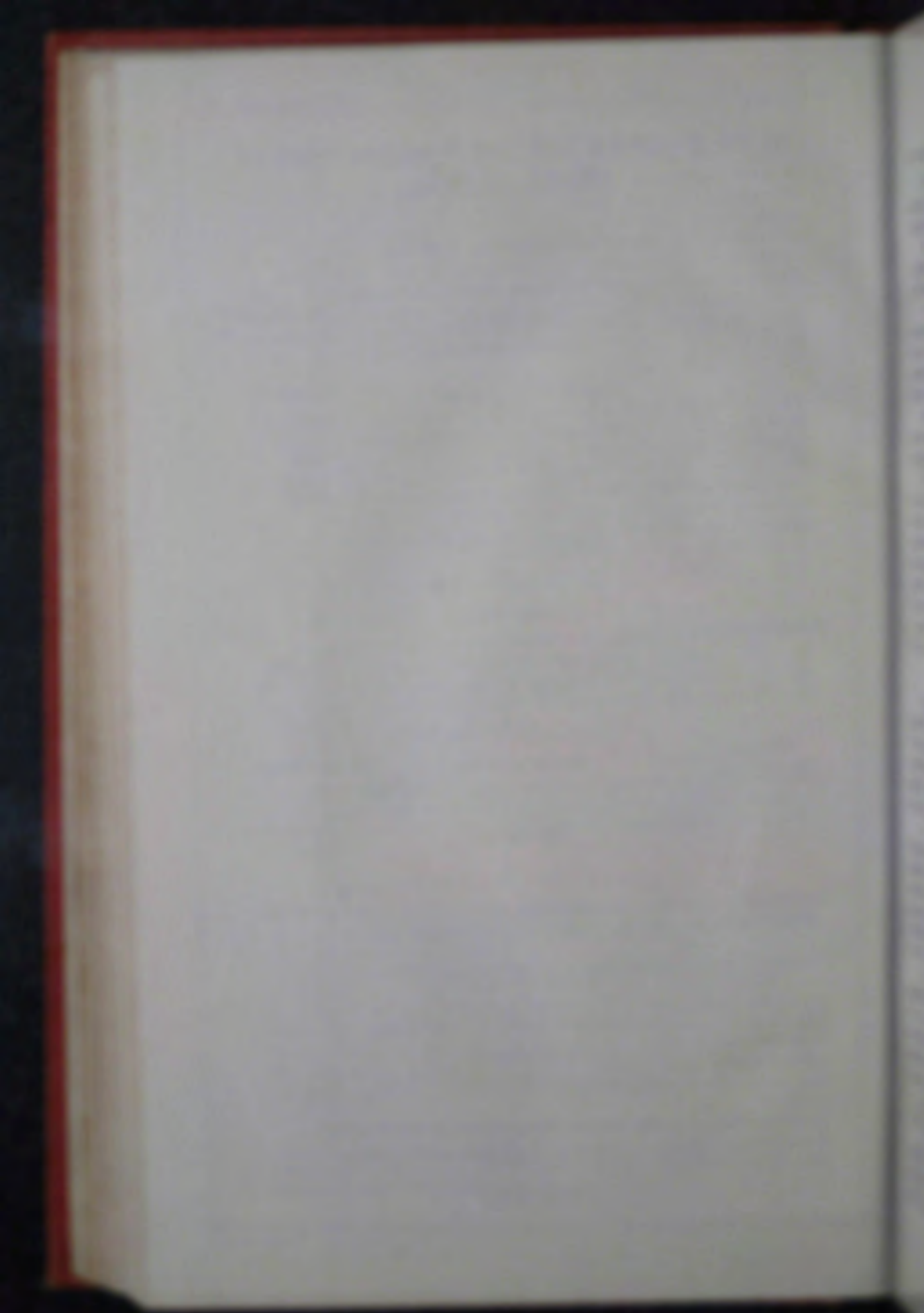
FLOW DIAGRAM FOR THE MANUFACTURE OF CRUDE TETRYL.

Dimethyl Aniline. (D.M.A.)

Sulphator. ← H₂ SO₄ 94% at about 30°C.

D.M.A. Sulphate.

Nitrator. ← HNO₃ 90% 2 Hours at about 70°C.

Tetryl + Waste Acid.

To Acid recovery. ← Quartz Filter.

Acid Tetryl.

Waste Washings. ← Drowning Pot. ← Water.

Wet Tetryl.

Waste Washings. ← Boiling Vat. ← Water.

Tetryl Sludge.

Waste Washings. ← Centrifugal.

Tetryl with about 5% moisture content, ready for purification and subsequent "corning."

FIG. 8·2.

Malby & Sons, Lith.

2. *Purification of the Crude Tetryl.*

The method of purification depends upon the Grade of the finished product. Purification is the only method of stabilising, no other materials being added for this purpose.

For Grade 2, the crude tetryl in a state of very fine division, is subjected to prolonged boiling and agitation in water, and is then centrifuged. This is the cheapest grade.

For Grade 1, the crude product is dissolved in acetone, in pans with mechanical stirrers. It is then passed through a filter to remove solid impurities, and precipitated in a fine state of division by the addition of water. It is collected, boiled, and centrifuged, as for Grade 2. The diluted acetone goes to the plant for acetone recovery.

Grade 1*a* is purified similarly to Grade 1, but nitric acid is used in the place of acetone, and is subsequently recovered. This process of purification, however, is obsolescent.

All the above grades are finally " corned." This is carried out to prevent injurious effects on the health of the workers, in whom tetryl, in a finely divided state, is liable to produce dermatitis. It consists in converting the fine crystalline or powdered product into very small pellets, by working up with a 1 per cent. solution of gum arabic, passing through a sieve of definite mesh, and finally drying. 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 fuzes 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 1*a* 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. 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).

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CHAPTER IX.

MIXED EXPLOSIVES.

</div>

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 to completely oxidise all the combustible material in it.

The most suitable oxidising 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 VII.

An outline of the manufacture of certain raw materials, and a description of a few of the explosive mixtures in which they are used will now be given. It is only possible to consider quite a small number of such mixtures in order to illustrate general types ; they are made commercially in endless variety.

Nitrates.

The natural deposits of sodium nitrate (chile saltpetre) and potassium nitrate (nitre, or saltpetre), have already been mentioned. Artificial nitre beds used also to be a source of saltpetre, but the supply from these, has been replaced by "conversion" saltpetre produced by the action of chile saltpetre on potassium chloride in hot solution ; the latter salt occurs in vast natural deposits in Germany.

$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl.$$
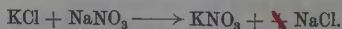
Sodium and potassium nitrates are purified by solution in boiling water, filtration, and recrystallisation. They are then dried, and finely ground.

Sodium and ammonium nitrates are very hygroscopic, and explosives containing either of these constituents must invariably be enclosed in a waterproof and gas-proof covering, for if such mixtures become damp, they will often fail to detonate, or explode.

Potassium nitrate is not hygroscopic. For this reason it is employed in gunpowders, rather than the much cheaper sodium nitrate.

Other nitrates commonly used in explosive and illuminating mixtures are those of barium and strontium. They are prepared by dissolving the sulphides or carbonates in nitric acid, or by the double decomposition of soluble barium or strontium salts with sodium nitrate.

Chlorates and Perchlorates.

Sodium chlorate and perchlorate are manufactured as a source of potassium chlorate, potassium perchlorate, and ammonium perchlorate, which are obtained from them by double decomposition with a soluble potassium or ammonium salt.

Sodium chlorate is too hygroscopic and ammonium chlorate too unstable, to be used much for explosive purposes.

Potassium chlorate is, however, an important ingredient of detonators and cap compositions; and ammonium perchlorate is the basis of many mixed high explosives. Both these salts are very rich in oxygen, which is comparatively readily liberated. Explosives containing either salt are much more sensitive to shock or friction than those containing nitrates, and this somewhat limits the field of their employment; but perchlorate mixtures are considerably more stable, in this respect, than those containing chlorates.

Sodium chlorate is made by the action of chlorine on a hot solution of sodium carbonate :—

$$3Na_2CO_3 + 3Cl_2 \longrightarrow NaClO_3 + 5NaCl + 3CO_2.$$

or by the electrolytic oxidation of a hot solution of common salt :—

$$NaCl + 3O \longrightarrow NaClO_3.$$

The chlorate is obtained by concentration and crystallisation from the solution.

Under suitable conditions the sodium chlorate solution can be further oxidised electrolytically to perchlorate :—

$$NaClO_3 + O \longrightarrow NaClO_4.$$

Potassium chlorate and ammonium perchlorate are readily prepared by double decomposition from the chloride and sulphate respectively, with sodium chlorate or perchlorate :—

$$KCl + NaClO_3 \longrightarrow KClO_3 + NaCl.$$
$$(NH_4)_2SO_4 + NaClO_4 \longrightarrow 2NH_4ClO_4 + Na_2SO_4.$$
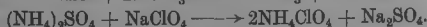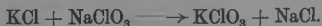
These may be compared with similar reactions for the manufacture of potassium and ammonium nitrates from the chloride and sulphate :—

$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl.$$
$$(NH_4)_2SO_4 + 2NaNO_3 \longrightarrow 2NH_4NO_3 + Na_2SO_4.$$

The chlorate, perchlorate, or nitrate, is obtained by concentration and crystallisation from the mother liquor containing it, and is then dried, and finely ground.

Ammonium perchlorate can be detonated by itself, but it is always mixed with other substances for explosive purposes, as it contains more oxygen than is necessary for the combustion of its own hydrogen. The production of hydrochloric acid by its detonation is in some ways disadvantageous.

Meta-dinitro-benzene and trinitro-meta-xylene are two nitro-compounds which have been used in certain mixed explosives :—

m-dinitro-benzene.
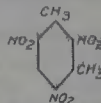
Trinitro-m-xylene.

They are made by the further nitration of nitro-benzene and mono-nitro-meta-xylene respectively, by a mixture of nitric and sulphuric acids. They are both solids, and can be detonated at maximum velocities of 6,100 and 6,600 metres per second respectively.

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 nitro-glycerine, 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 dinitroglycerine, 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 com-bustion, it is unnecessary to add any further oxidising agent. Nearly all dynamites contain a small proportion or calcium or magnesium carbonate as a stabiliser.

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 to completely oxidise all combustible material.

Other types contain soluble nitrocellulose in the place of wood meal or charcoal. These form a " gelatinised " 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 9.A.

PERCENTAGE COMPOSITION OF BLASTING GELATINE, GELIGNITE, AND GELATINE DYNAMITE.

	Blasting Gelatine.	Gelignite.	Gelatine Dynamite.
Nitroglycerine	91·5	60·5	74·5
Collodion cotton (soluble nitrocellulose)	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 stabiliser, which serves to neutralise 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.

AMMONAL.

Composition.

Ammonium nitrate	65
T.N.T.	15
Aluminium powder (coarse)	16
Aluminium powder (fine)	1
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 has been extensively used for filling bombs and grenades, but is being replaced for this purpose by amatol and alumatol ; the latter being a very similar type of explosive, containing no charcoal, and a lower percentage of aluminium.

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 is used as a bomb and grenade filling.

PICRAMITE.

Composition.

Ammonium nitrate	..	..	..	..	72
Ammonium picrate	..	..	..	..	28

Properties and Uses.

A yellow powder, which is hygroscopic, and non-poisonous. 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 is used for grenades and bombs, into which it is 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.

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 is thus limited to fillings for bombs and grenades, which will not be subjected to severe shock. It is a fine dark brown powder, whose composition renders it waterproof. The addition of mineral jelly reduces its sensitiveness to shock or friction.

<div align="center">BLASTINE.</div>

Composition.

Ammonium perchlorate	..	..	..	63
Sodium nitrate ..	..	..	..	23
Dinitro-toluene ..	..	..	..	8
Paraffin wax ..	..	..	..	6

Properties and Uses.

A hygroscopic high explosive 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 :—

	R.D. COMPOSITION "B."	R.D. COMPOSITION No. 30.
Ammonium perchlorate ..	80	78
Wood meal ..	5	—
Aluminium powder ..	—	6
Paraffin wax ..	15	16
	White, or faint brown granules.	Soft, silver-white granules.

Composition. (heading appears left of table)

Properties and Uses.

Both are 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.

<div align="center">TONITE.</div>

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 sensitive to percussion or friction. It should not be stored at a temperature greater than 120° F.

BARATOL.

Composition.

Barium nitrate ..	..	..	..	..	20
T.N.T. ..	..	..	..	..	80

Properties.

A high explosive that is not hygroscopic, and not materially affected by high temperatures of storage; it can thus be used in the tropics without loss of detonating properties. It is used as a grenade filling, and to a certain extent as a substitute for guncotton.

BELLITE.

A mixture of 83 per cent. of ammonium nitrate, with 17 per cent. of dinitro-benzene, has been used for filling bombs and grenades.

SONITE.

A mixture of guncotton and soluble " nitrocellulose " with 1 per cent. of mineral jelly, gelatinised 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, its use being 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.

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.

PRIMING COMPOSITION, containing some 25 per cent. of magnesium powder mixed with barium and potassium nitrates, and 75 per cent. of gunpowder size 3, is used with certain shell fillings (*e.g.*, incendiary mixtures, etc.) in cases where the flash from the magazine of the ordinary fuze is not found to be sufficient to ensure ignition. All mixtures containing magnesium powder and oxidising agents must be handled with great care, as they are most sensitive to friction.

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

CHAPTER X.

GUNPOWDER, SLOWMATCH, QUICKMATCH, AND FUZE COMPOSITION.

GUNPOWDER.

Introduction.

Gunpowder is the oldest explosive in existence, and its origin is entirely unknown. A brief résumé of its history is given in Chapter III.

It is still important as an explosive, though that importance is of a secondary nature. As a propellant, for use in the Service, it is obsolete.

Gunpowder consists of *charcoal*, *saltpetre* and *sulphur*, in various proportions. It is a mechanical mixture ; in which respect it differs from explosives such as the cordites 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. This was the great disadvantage of gunpowder as a propellant, apart from others, as the solid products caused rapid fouling of the weapons, and constituted huge clouds of dense white smoke on discharge.

RAW MATERIALS AND THEIR MANUFACTURE.

1. *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 $1\frac{1}{2}$ 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 $3\frac{1}{2}$ to

6 hours. The volatile products of distillation escape by the delivery pipe, and are either collected for by-product recovery, or are used as gas to assist in heating the furnaces.

(ii) The cylinder and its contents are then removed from the furnace and allowed to cool out of contact with air. 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 39 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. ; and ash, 2 per cent.

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.

2. *Saltpetre.* (KNO_3) —(i) Saltpetre is found native in India, where large quantities are recovered from the soil of certain localities by the inhabitants. The soil is lixiviated with water, and the solution concentrated by boiling. Crude saltpetre containing about 90 per cent. KNO_3 is obtained by crystallisation, and is then exported to this country. It is further purified by recrystallisation before it is suitable for use in gunpowder.

(ii) Saltpetre can also be obtained by a conversion reaction between sodium nitrate and potassium chloride. The sodium nitrate is used in the form of Chile nitrate ; and the potassium chloride occurs as a double chloride of potassium and magnesium in the mineral *Carnallite,* of which there are large deposits at Stassfurt, Germany.

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. The potassium nitrate so obtained contains a certain amount of sodium chloride and about ·5 per cent magnesium chloride

$$KCl + NaNO_3 \longrightarrow NaCl + KNO_3$$
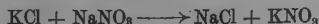
The percentage of chloride can be reduced to about ·05 by further recrystallisation from solutions in some of the wash liquors, and the purified saltpetre is finally dried.

During the final crystallisation, the solution is vigorously agitated in order to obtain the saltpetre in as fine a form as possible. This

F

eliminates the necessity for grinding before the saltpetre is incorporated in the powder.

3. *Sulphur.*—Sulphur occurs as native deposits of volcanic origin in Sicily and America. It is also obtained by chemical methods from calcium sulphides.

(i) Sulphur from Sicily. Volcanic sulphur occurs native in Sicily as an ore in which it is mixed with limestone. The ore contains from 20 to 40 per cent. of sulphur. It is recovered from the ore by burning or heating. The sulphur melts, is run out and collected. It is finally purified by distillation.

(ii) American Sulphur (Frasch process).—A limestone ore containing about 70 per cent. of sulphur is found at depths of about 500 feet in Louisiana (U.S.A.). The deposit is covered by extensive quicksands which prohibit normal mining methods. Borings are sunk, and superheated water forced down. Under its action the sulphur is melted. The molten sulphur is blown to the surface by compressed air. It is there collected, and in this state contains about 0.03 per cent. of impurity.

The purification of sulphur by distillation has been referred to in (i) above. This gives sulphur in two forms: (*a*) by sublimation "flowers" of sulphur; and (*b*) "roll" sulphur. The former is entirely unsuitable for use in gunpowder, as it contains an appreciable quantity of sulphuric acid. The roll sulphur is sufficiently pure, and only needs grinding.

Roll sulphur is a pale yellow crystalline solid. It melts at 113° C. but on further heating it becomes gradually darker in colour and considerably more viscous. It is practically solid between 160° and 220° C. It boils at $444.5°$ C., and ignites at 261° C.

Manufacture of Gunpowder.

Only ~~four~~ *five* grades of gunpowder are being retained in the Service. These are:—

Size 1 .. For pebble *(P.3)* powder. Passing sieve apertures of $.75$ in. – $.375$ in.

Size 2 .. For granulated powder (G.~~7~~ *6*). Passing sieve apertures of $.25$ in. – ·~~10~~ in.

Size 3 .. For granulated powder (G.12). Passing sieve apertures of IMM Standard ~~5—10~~. *6 – 12*

Size 4 .. For granulated powder (G.20). Passing sieve apertures of IMM Standard ~~10~~ *12* – 20.

Sizes 2, 3, 4 ~~The last three sizes~~ correspond to R.L.G.², R.F.G.² and R.P.P. of the old nomenclature. *Mealed powder, passing sieve apertures of I.M.M. Standard 120-200.*

The manufacture may be divided into various operations, *e.g.*, Grinding, Incorporating, &c.

1. *Grinding.*—The three ingredients are ground separately, the state of division being controlled by sifting through sieves of appropriate mesh.
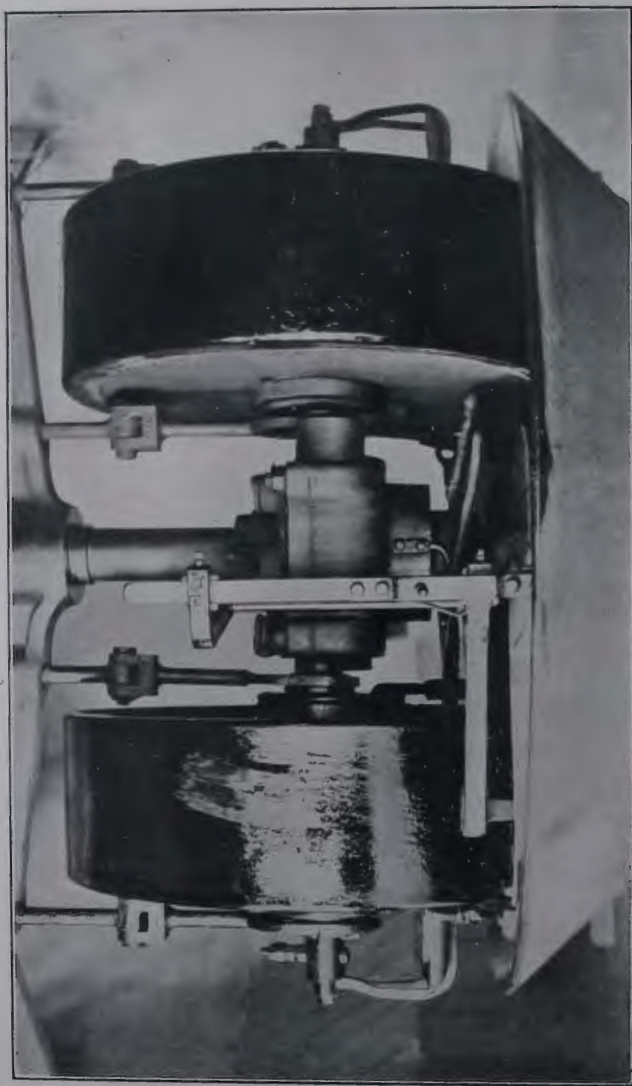
Fig. 10.1.—Gunpowder Incorporator Mill.

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 appreciable amount of moisture that is usually contained in it.

3. *Preliminary Mixing.*—The ingredients are placed in a cylindrical drum on the axis 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, as the presence of large hard particles in the subsequent operations may 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. 10.1) the runners are supported in such a manner that there is a small clearance between them and the iron bed-plate on which they run. They are also capable of slight independent movement in a vertical direction.

The older mills had stone or iron runners which were not suspended. These are still in use.

Two wooden ploughs rotate with the edge-runners. They stir up the charge, and prevent it accumulating at the centre or curb of the bed-plate.

The mills are isolated by strong masonry walls, and the danger of explosion during milling is minimised by keeping the charge damp. No one is allowed in the milling house once the operation has started. Automatic drowning arrangements are provided for each mill.

Incorporation is important ; long incorporation gives a uniform and quick burning powder. 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.

The product, after milling, is known as " mill-cake."

5. *Breaking Down.*—The mill-cake is often found to adhere to the bed-plate of the mill in hard masses. It is removed by the application of water, and the careful use of a wooden instrument if necessary. 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 press operated hydraulically. The powder is not usually confined in any container during this operation owing to the danger of friction against the sides. This is a dangerous part of the manufacture of gunpowder, each press being carefully isolated, and no one is allowed in the building during " pressing," the necessary controls for the mills being contained in a separate building separated from the press-house by a mound.

The product is known as " press-cake."

7. *Granulating (or Corning).* — The press-cake is passed through a series of rollers which break it up. 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 renders the surface less porous, and so impedes 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.

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 with the evolution of large quantities of white smoke. It cannot be detonated, as it is only a mechanical mixture and the constitutents are not, in themselves, explosive.

It is quite stable in storage. Moisture affects it, as it renders it more difficult to ignite, and it may also remove some of the saltpetre. The effect of moisture 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 65 (picric acid = 100). The violence of the explosion of gunpowder can be varied in many ways. It may be made slower burning by decreasing the percentage of saltpetre, compressing it 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 solids are chiefly potassium carbonate, potassium sulphate and potassium thiocyanate, with a small quantity of potassium sulphide, and trace 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.

(e) Capacity for absorbing moisture.

(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 compositions, e.g., quickmatch, priming and cap compositions.

(vi) Bursting charges of some shell, e.g., shrapnel.

It is much used commercially for demolition and blasting purposes.

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 boiled with a solution of mealed gunpowder and gum. Before it is quite dry, it is dusted with mealed gunpowder. It is usually issued enclosed in a tube of paper or calico, in which form it is known as a " leader."

Unenclosed it burns at the rate of 1 yard in 13 seconds. The enclosed form burns very much more rapidly. It is largely used for priming rockets, detonators, etc.

INSTANTANEOUS 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 covering of twisted cotton. The whole is enclosed in a gutta-percha tube, which is braided with worsted on the exterior. It is varnished orange or yellow. The colour, and the worsted braiding serve to distinguish it, both to the eye and to the touch, from safety fuze.

It burns at the rate of 30 yards a second. It is easily ignited by a portfire or vesuvian, but it should not be held in the hand while so doing.

SAFETY FUZE.

Safety Fuze No. 9, Mark II/C/ consists of a train of fine grain powder enclosed in jute yarn. The whole is contained in a flexible tube of waterproof composition encased in waterproof tape. Its external colour is black.

It burns at the rate of 1 yard in 75 to 105 seconds.

TIME-FUZE COMPOSITIONS.

Compositions for use in the time rings of fuzes have the approximate constitution given below :—

Potassium nitrate	74–76
Sulphur	$8–10\frac{1}{2}$
Charcoal	$18–13\frac{1}{2}$

The composition is 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 time of burning varies inversely as the time of milling up to a maximum time of milling of 12 hours. Milling for any longer period has no effect on the time 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. Lignum vitæ is a hard wood, the charcoal from which is 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 a 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.

NITRATOR — SEPARATOR.

FIGURE II. I.

Malby&Sons.Lith.
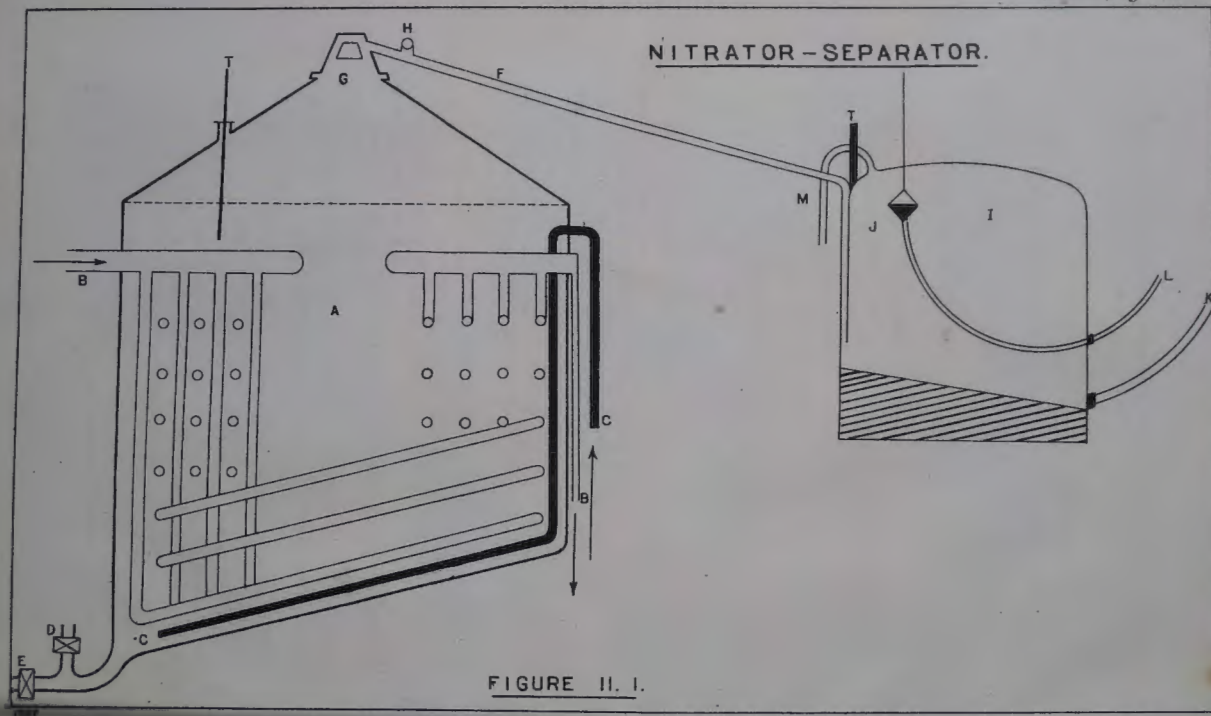
From the results obtained, it is evident that the factors affecting the successful operations of a time fuze, are (a) External and (b) Internal.

(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 for further details.

As regards (b) more may be said here. In the case of a fuze composition the products of combustion of which are not entirely gaseous, a slag is formed. This slag, under the action of the rotation of the projectile, is liable to choke the ring vents, so giving rise to fluctuating pressures which lead to irregularity of burning and blinds. These effects are particularly noticeable when the slag is of a fluid or plastic nature. The fluidity of the slag seems to be a function of the sulphur content of the composition, and for this reason fuze compositions should not contain more than 10 per cent. sulphur.

Attempts have been made to produce slagless compositions ; one of the most successful being Research Department Composition No. 202 (see page 79.)

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.

———————

Chapter XI.

NITROGLYCERINE.

Introduction.

Nitroglycerine was discovered by Sobrero in 1846, and its manufacture on a commercial scale was commenced in Sweden about fifteen years later. It is not a nitro-compound, as its name would imply, but a simple nitric ester, glyceryl trinitrate.

Glycerol (glycerine) is a trihydric alcohol which is obtained from fats and oils in the process of soap-boiling. These are esters of glycerol and fatty acids, and yield glycerol and soaps when boiled with an alkali. Taking glyceryl tristearate (which occurs in many fats)

as a typical example, the chemical reaction may be represented as follows :—

$$
\begin{array}{l}
CH_2COOC_{17}H_{35} \\
\;\big| \\
CHCOOC_{17}H_{35} + 3NaOH \longrightarrow \\
\;\big| \\
CH_2COOC_{17}H_{35}
\end{array}
\qquad
\begin{array}{l}
CH_2OH \\
\;\big| \\
CHOH + 3C_{17}H_{35}COONa \\
\;\big| \\
CH_2OH
\end{array}
$$

Glyceryl Tristearate.   (A Fat.)   Glycerol.   (A Soap.)
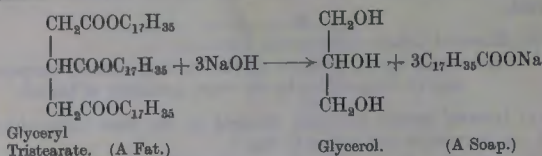
Most common fats, and whale oil, are manufacturing sources of glycerol, which is a common article of commerce. From these it is obtained by soap-boiling ; by hydrolysis with water under pressure in the presence of a catalyst ; or by the action of superheated steam.

Glyceryl trinitrate is readily formed by the action of nitric acid upon glycerol :—

$$
\begin{array}{l}
CH_2OH \\
\;\big| \\
CHOH + 3HNO_3 \longrightarrow \\
\;\big| \\
CH_2OH
\end{array}
\qquad
\begin{array}{l}
CH_2ONO_2 \\
\;\big| \\
CHONO_2 + 3H_2O \\
\;\big| \\
CH_2ONO_2
\end{array}
$$

Glycerol.   Glyceryl Trinitrate or Nitroglycerine.
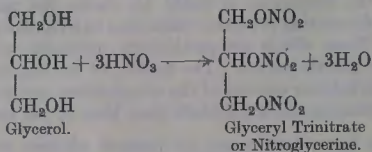
If the above molecular proportions are used, the reaction will not proceed to completion, owing to the dilution of the nitric. acid by the water formed. In manufacture this is removed as rapidly as it is formed by the addition of sulphuric acid to the nitric acid used for nitration. The action then proceeds very readily, and with a considerable evolution of heat.

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

$$ 2C_3H_5(NO_3)_3 \longrightarrow 6CO_2 + 5H_2O + 3N_2 + O $$
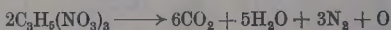
As a nitrate, nitroglycerine is unique, in that it contains more than enough oxygen for its complete combustion.

Owing to its great sensitiveness, nitroglycerine can neither be pumped through pipes, nor its flow controlled through stop-cocks with any degree of safety. In manufacture it is passed from vessel to vessel in covered lead gutters, connected when necessary by hose piping, 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.

The following is an outline of the process of manufacture, considered in its various stages.

(a) *Nitration.*

The nitration of the glycerol is carried out in the nitrator-separator of Rintoul and Thomson, a diagram of which is given in Fig. 11.1.

FLOW DIAGRAM FOR THE MANUFACTURE OF "NITROGLYCERINE".

Glycerine
(0·44 Ton)

Waste Acid
used for displacement

going eventually to Acid
recovery plant

Nitrator Separator
(45 Mins. for nitration)
(20 Mins. for separation)

Nitrating
Acid
(2·6 Tons)

59% H_2SO_4
39% HNO_3
2% H_2O

Drowning
Tank

Acid "Nitroglycerine"

Waste
Washings

Settling
Tank

Labyrinth

Wash
Water

Washing Tanks

Water; or
Sodium Carbonate Solution

Wet "Nitroglycerine"

Sponge Filter

Dry "Nitroglycerine"

FIG. II·2.

1507.

Malby & Sons, Lith.

Fig. 11.3.—Interior of Nitrator House, showing Nitrator-Separator.

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 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 0·44 tons of glycerol, producing about 1 ton 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. ; should this temperature 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 forty-five 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 twenty 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, part of it being used for the displacement of a subsequent charge, and part going to the acid recovery plant, where

the nitric and sulphuric acids are separated and recovered. 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 localise 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.

(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 a fourth time 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 nitro-glycerine 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.

The nitroglycerine is now very slightly alkaline. It is finally run through a sponge filter to remove the last traces of water, subjected to the heat test (*see* p. 125), 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. 11.2. presents the manufacturing processes in the form of a flow diagram.

PROPERTIES AND USES.

Nitroglycerine is a colourless oily liquid of sp. gr. 1·6 which is insoluble in water, but soluble in alcohol, acetone, ether, &c. It is very poisonous, giving rise to violent headache, even by the absorption of minute quantities through the skin. Workers in factories, however, soon become inured to its effects, and are no longer troubled by them.

It is slightly volatile, decomposes before boiling, and ignites at about 180° C., burning quietly with a flame whose edges are tinged with green.

Its use is somewhat restricted by its sensitiveness and its liquid condition. It 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 neutralised by some stabiliser.

In the solid state it can exist in two crystalline forms. The normal rhombic form with a melting point of about 13° C. is comparatively stable; whilst the triclinic form melts at about 2° C. and is much more sensitive. The latter has probably been the cause of many accidents which have occurred during the thawing of dynamites.

It is a most powerful explosive with a maximum velocity of detonation of 8,000 metres per second, and is very sensitive to impact or friction.

Nitroglycerine 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 propellants of the cordite type.

Dinitroglycerine.

From its chemical formula it is seen that glycerol can form two dinitrates.

$$CH_2ONO_2 \qquad\qquad CH_2ONO_2$$
$$|\qquad\qquad\qquad\qquad |$$
$$CHOH \qquad\qquad\quad CHONO_2$$
$$|\qquad\qquad\qquad\qquad |$$
$$CH_2ONO_2 \qquad\qquad CH_2OH$$

<div align="center">

Symmetrical   Unsymmetrical
Glyceryl Dinitrate.   Glyceryl Dinitrate.

</div>
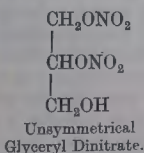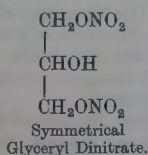
A mixture of these can be obtained by the hydrolysis of the trinitrate by moderately strong sulphuric acid. This mixture is sometimes added to nitroglycerine (for making dynamites, &c.) in order to lower its freezing point.

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 Pelouze 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. Its 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 *not* 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 $13 \cdot 9$ per cent. Nitrocellulose corresponding to the tri-nitrate ($14 \cdot 14$ per cent. N.) has not, so far, been prepared.

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

RAW MATERIAL AND ITS PREPARATION.

Cellulose.

Cellulose is the main constituent of the cell walls in vegetable tissue. It is a very complex substance, having the formula $(C_6H_{10}O_5)_n$.

TABLE 12.A.

Composition.	Per cent. N.	Use.	Stability.	Solubility.		
				Water, and most Organic Solvents.	Acetone.	Ether Alcohol.
Trinitrate ...	14·14	—	—	Insoluble	Soluble	Insoluble
	13·9	Highest obtainable : not used ...　...	V. Bad	,,	,,	,,
	13·5	Highest stable nitrate ...　...　...	Fair	,,	,,	,,
	13·1 to 12·8	Manufacture of " G/C "　...　... Cordite Mk. I. ,,　M.D. Ballistite.	Good	,,	,,	,,
	12·3 to 12·1	Manufacture of R.D.B. ...　...　... Ballistite. N.C.T. Blasting gelatine. Ardeer type propellants.	,, ,,	,, ,,	,, ,,	Soluble. ,,
Dinitrate ...	11·1	—	—	,,	,,	,,

The value of n cannot be stated definitely, but it seems improbable that it is ever less than 4.

There are several types of cellulose differing in chemical behaviour and composition. These different types may be grouped into two main categories :—

1. Hemi- or β-Cellulose.
2. Normal, α- or Resistant Cellulose.

The latter is the most important, as it is the cellulose required for explosives manufacture.

Hemi- or β-Cellulose.

This is distinguishable from the α-variety by its higher reactivity. It is reactive to weak reagents and it is soluble in a 3 per cent. solution of caustic soda (NaOH). Under this class, many Celluloses could be discussed, but it is sufficient for the present purpose to say that they usually form unstable nitrates and are therefore undesirable. The same applies 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 a solution of caustic soda (NaOH), α-cellulose changes over 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 similar mild oxidising agent, increases the percentage of oxygen in the cellulose, and transforms it to *oxycellulose*. This substance is again more reactive, 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 and water.

(v*a*) Strong sulphuric acid will form a sulphuric ester of α-cellulose, but considerable charring takes place at the same time.

(v*b*) With dilute sulphuric acid, the α-cellulose is transformed to a sugar ($C_6H_{12}O_6$).

Action of Nitric Acid.

Table 12.A shows the different percentages of nitrogen in nitrocellulose used for explosives. In general the nitrogen content can be controlled by the amount of water in the original mixed acid.

The lower nitrates are much used in commerce for the manufacture of substances such as pyroxylin, celluloid, collodion, etc., as they are readily soluble in many organic solvents.

FIG. 12.1.

Photomicrograph of Cotton Cellulose.
× 100.

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.

Some processes for making artificial silk are based on the solubility of the lower nitrates of cellulose. The nitrated cellulose is dissolved in a volatile solvent, and the solution is then squirted through a fine die. The solvent evaporates almost immediately, and leaves a thread of nitrocellulose. This then undergoes further treatment in order to convert it to non-explosive cellulose, which is used as " artificial silk."

α-cellulose is soluble in a few reagents. It is directly soluble in a solution of copper hydroxide in ammonia (Schweitzer's Reagent), and also in a solution of zinc chloride in hydrochloric acid. 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 :—1, Cotton, 2, wood, and 3, annual plants.

1. *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 cleansing and picking, forms the raw material of the cotton industry.

Cotton cellulose is a white fibrous substance. Under the microscope the fibres appear like a flat twisted tube.

Fig. 12.1, which is a photomicrograph, plainly shows this twisted structure.

For explosive purposes, cotton is used in two forms : For Naval purposes, only the best cotton sliver (unspun carded cotton) is permissible ; for Military use, the best cotton waste is considered suitable.

Specifications lay down the sources from which it may be supplied, and the tests and limits of impurity with which the material must comply before acceptance. The following quotation is taken from one of these specifications :—

" *Definition.*—The cotton cellulose as finally prepared for nitration should be in the form of free fibre, and may contain loose thread and well-opened cop, and must not contain woven thread nor fine cotton dust.

" *Preparation.*—The bales of raw cotton waste to be picked free from gross foreign impurities and passed through an opening machine to disintegrate completely all felted or helically wound masses. The cotton would be degreased if necessary. The cotton, during transit ....is to be packed in suitable packages, which are not liable to damage on transit, thus exposing the cotton to risk of contamination................. The cotton to be subjected to inspection ....throughout all the operation.

" The cotton is to be boiled in a rotating kier with 3 per cent. solution of sodium hydroxide................. Boiling is to be continued for 10 hours at a steam pressure of 40 lbs. to the square inch.

" .... At the end of this treatment.....................the cooled cotton.................should be washed with cold water..................... dried at 95° to 105° C. tested and baled.

" *Tests.*—The finished cotton to be free from gross impurities and to give
values not greater than the following :—

		Per cent.
Moisture...		8·0
Soluble in ether		0·5
Soluble in 100 parts of boiling 3 per cent. sodium hydroxide		3·0
Mineral matter		0·8
Absolute viscosity of a 2 per cent. solution in "cuprammonium" (Schweitzer's reagent)		50·0

" Except as regards the above figures it must be entirely free from
organic matter other than pure resistant normal cellulose. The
purified waste when dyed by the Malachite Green Test shall not
contain an amount of ligneous impurity greater than that present in
the standard sample held by the War Department Chemist,
Woolwich."

2. *Wood Cellulose.*

When the Great War accentuated the need for indigenous
sources of supply, attention was drawn to the possibility of replacing
cotton, as a source of cellulose, by wood. 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, though
the majority of the wood pulp is imported. This, however, is not so
serious a drawback as it is with cotton, since Norway and Sweden,
from which the majority of the pulp is imported, are very close to our
shores. 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 subjected to the action
of either caustic soda (NaOH) or calcium bisulphite ($Ca(HSO_3)_2$) in a
high-pressure boiler. The major portion of the impurities is thereby
removed, and the wood is reduced to a pulp. The 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.

(*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 thoroughly
washing with water.

Wood cellulose may be nitrated either in a loose fibrous form or
in the form of thin paper. In the former case, it is usually made
into a thick cardboard for convenience in handling and storage, and

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

Cotton in Bales
↓
| Bale Breakers |

| Picking Tables | Preliminary Treatment

| Mechanical Teaser |

| Drier |

Nitration.

Waste Acid to Recovery ← | Nitrators | ← Mixed Acid

after Nitration, displacement of Acid by water.

1 Acid Boil.
5 Water Boils
1 Alkaline Boil. | Boiling Vats |

| Beaters |

| Grit trap, Blanket and Magnet runs. |

Sample for Alkalinity Test ← | Potchers | Purification

| Blending Tanks |

| Hydraulic Presses |

Guncotton Cylinders to Storage

FIG. 12.2.

subsequently disintegrated prior to nitration. In the latter case the pulp is made into a thin crinkled paper, strict attention being 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.

The subsequent treatment of the cellulose during nitration and after does not differ in principle from the methods at present employed for the nitration of cotton.

3. Cellulose from Annuals.

Annuals such as flax, artichokes, etc., contain appreciable quantities of cellulose, which is obtainable in a form suitable for the manufacture of nitrocellulose by methods which are essentially similar to those employed in the case of wood.

It is unlikely, at present, that this source of cellulose will attain any importance except to augment other supplies in case of war emergency.

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 solvent such as benzol.

    (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. Cellulose other than normal cellulose.

    Boiling with a 3 per cent. solution of caustic soda will dissolve out these substances. Formerly further purification was attempted by bleaching the cotton with bleaching powder, but this was found to result in the formation of oxycellulose, which had then to be eliminated.

It is essential that only α-cellulose should remain in the final material for nitration, if a stable product is to be obtained.

Before cellulose can be accepted for nitration, certain tests are applied as laid down in the service specifications. They are approximately seven in number.

    1 Moisture content. This should not exceed about 8 per cent.

    2. To estimate the amount of oily or greasy matter present, the cellulose is extracted with ether, and the percentage of matter so removed is estimated.

    3. The presence of celluloses other than α-cellulose is detected by estimating the percentage soluble in a 3 per cent. solution of caustic soda (NaOH) after boiling for one hour.

4. The ash content is taken as evidence of the percentage of inorganic impurity present.

5. Due to various causes, there is a possibility of starch being present in the cellulose. It is undesirable, as the esters formed by it with nitric acid are not stable. The cellulose is treated with a solution of potassium iodide, and if a blue colouration ensues, then starch is present, and a quantitative estimation is necessary.

6. The presence of wood fibre in the cellulose is detected by dyeing the material with malachite green. On bleaching, the cellulose becomes colourless, but the particles of wood remain unaffected, and show up as dark green specks on a white background. The test is made comparative by examining the specimen in conjunction with an accepted standard, kept by the War Department Chemist at Woolwich.

7. A further test, which was introduced during the Great War is the determination of the absolute viscosity of a 2 per cent. solution of the cellulose in Schweitzer's Reagent. The various solutions are made under standard conditions laid down in the specifications, and the viscosity is found by the "falling sphere" method. This test has for its object a comparative estimation of the molecular size of the cellulose in the sample.

The Manufacture of Nitrocellulose.

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

$$C_6H_{10}O_5 + xHNO_3 \longrightarrow C_6H_{(10-x)}O_{(5-x)}(NO_3)_x + xH_2O.$$
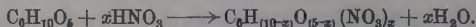
The value of "x" varies according to the conditions of nitration, viz., (i) temperature, (ii) time of nitration, and (iii) percentage of water present in the mixed acids. An increase in (i) and (iii) gives a lower, and an increase in (ii) a higher value to "x."

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 :—

	M.D.	R.D.B.
Sulphuric acid	71	62
Nitric acid	21	24
Water	8	14

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

A flow diagram of the method of nitration now to be described will be found in Fig. 12.2.

The nitration of cotton cellulose is here considered.
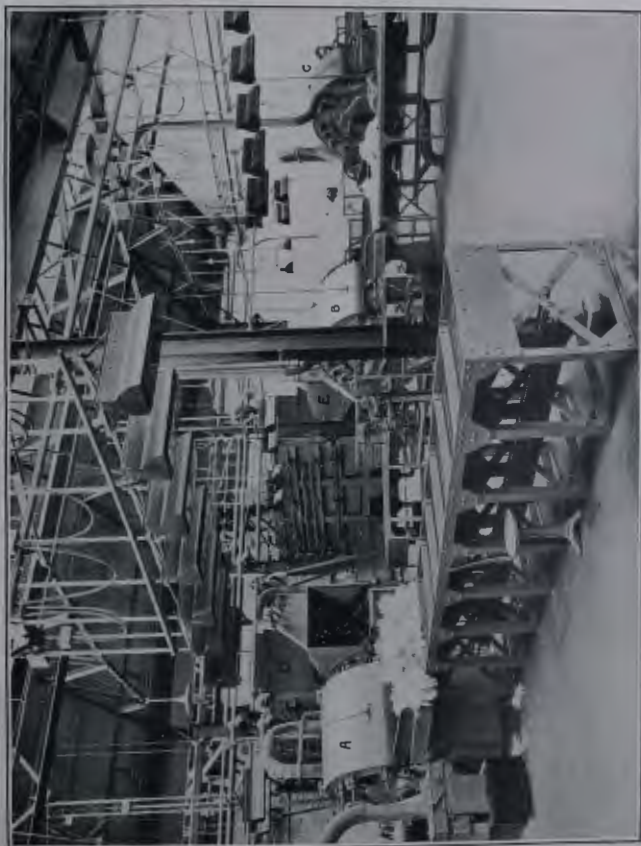
FIG. 12.3.

Machines for the Preliminary Treatment of Cotton Cellulose.
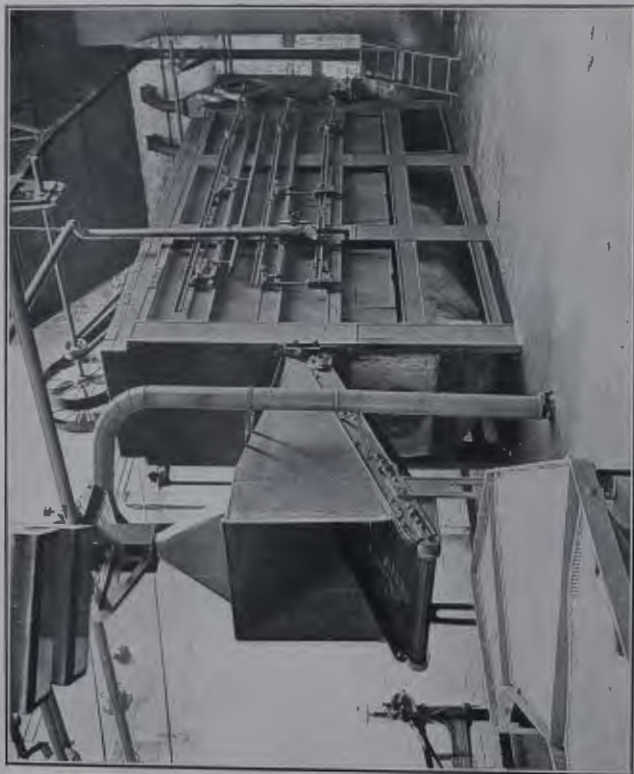
Fig. 12.4.
Cotton Drier.

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. 12.3, 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. 12.4.)

(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. 12.3. 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.

(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 lbs. to a charge, and conveyed to the nitrators.

2. *Nitration.*

(i) Nitration is performed in stoneware Nathan and Thompson displacement pans (Fig. 12.5), which are arranged in sets, four pans to a set. The interior of a cotton nitration house is shown in Fig. 12.6. 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. Aluminium paddles are used to push the cotton under the surface of the acid. When

G 2

immersion is complete the cotton is covered over with stone ware 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 $2\frac{1}{2}$ hours, and the temperature 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
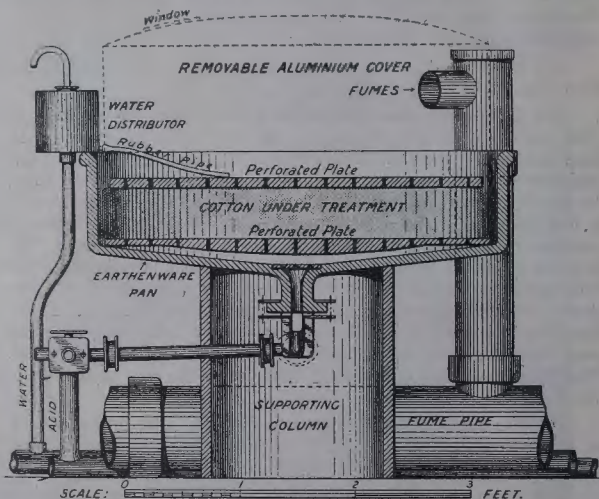
FIG. 12.5.—Section of Displacement Nitrator. (Manufacture of Nitrocellulose.)
From *Arms and Explosives*.

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 two mains for strong and weak displacement acid can be seen at D.
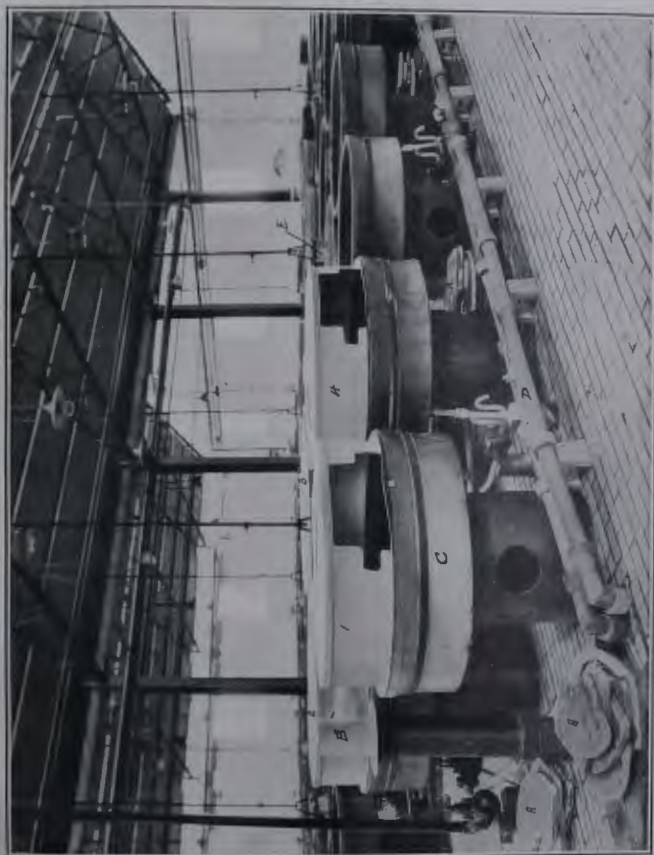
FIG. 12.6.   (Manufacture of Nitrocellulose.)

Nitration House.
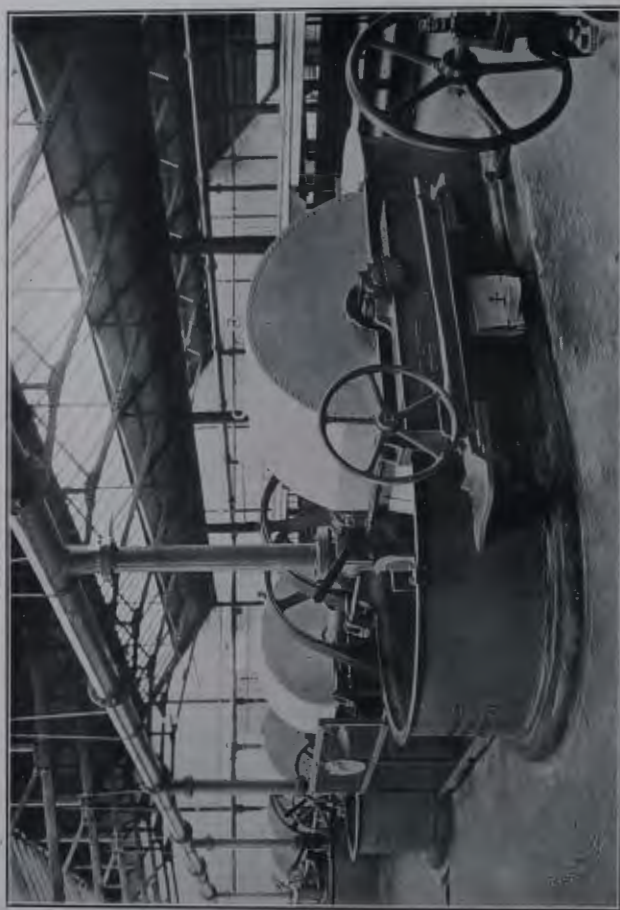
FIG. 12.7.—Beaters.

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.

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 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 1 per cent. acid in this first boil is sufficient to hydrolyse 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.

(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. 12.7) in which it is agitated for two hours between rapidly rotating knives. A battery of beaters is visible in the background of Fig. 12.8, numbered 1 to 6. The nitrocellulose leaves the beaters as a fine suspension in water.

(iii) From the previous operation, the nitrocellulose flows into a small tank fitted with a vertical baffle. This tank acts as a grit trap, and from it, the nitrocellulose overflows on 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. 12.8 at A, A, A.

(iv) By means of the gutter C, C, C (Fig. 12.8) 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.

(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 "primers" about 2 inches in diameter by 6 incles long, in a hydraulic moulding press. In this condition it is transported to magazines, where it is kept in a moist condition until required.

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 lbs. of acid and 32 lbs. 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., M.D., and M.C., and as a high explosive for demolitions.

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

Fig. 12.8.

Purification House. (Manufacture of Nitrocellulose.)

water being added if necessary. Sodium phenate ($C_6H_5O.Na$) 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 gelatinises 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 stabiliser in guncotton by neutralising 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 temperatures 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 gelatinisation 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 the war-heads of torpedoes, mines, &c.

CHAPTER XIII.

CORDITES, N.C.T. AND BALLISTITE.

Table 13.A gives the composition and properties of the substances which have been used in this country as propellants at one time or another. In this chapter the various types of *cordite*, *N.C.T.* (nitro-cellulose tubular) and *ballistite* are considered.

CORDITE.

Introduction.

This is the name applied in this country to a group of propellants which consist essentially of a uniform colloidal mixture of nitrocellulose and nitroglycerine with the addition of a stabiliser. The propellant is usually employed in the form of sticks or cords (whence the nomenclature), 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, potassium nitrate, barium nitrate and some colouring matter. The powder was partially gelatinised 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 (Vieille 1884) partially overcame this difficulty with their poudre B, which consisted of nitrocellulose gelatinised with

TABLE 13.A.

PROPELLANTS.

Propellant.	Per cent. Composition.			Nature of Stabiliser.	Per cent. N in N/C.	Physical Properties.	Heat evolved Cals./gram. (water gaseous).	Vol. gas at N.T.P. c.c.s./ gm.	Notes.
	N/C.	N/G.	Stabiliser, &c.						
Cordite, Mark I ...	37	58	5	Mineral Jelly ...	13·0 – *13·1*	Soft, easily marked by finger nail.	1·114	886	Very erosive.
Cordite, M.D. ... Cordite, M.C.... ...	65	30	5	Mineral Jelly ... "Cracked" M.J. ...	~~13·0~~ *12·9 – 13·2*	Hard, smooth ... Horny, brittle ...	0·939	933	Less erosive. Less N/G, therefore more propellant needed.
Cordite, R.D.B. ...	52	42	6	Mineral Jelly ...	12·2	Rough. Not brittle. Between Mark I and M.D.	0·904	959	More N/G compensated by low N in N/C and more M.J.
Ballistite "A" ...	60	40	Trace of Diphenyl-amine.	Diphenylamine ...	12·6 and 13·2	—	1·136	800	Erosive.
~~N.C.T.~~ { N.C.T. ...	99·5	—	0·5	Diphenylamine ...	12·6	—	0·777	961	—
~~Dupont S.A.~~	93·5	—	~~6·5*~~ *·6*	,,	12·6 and 13·2	—	~~0·777~~	~~961~~	—
N.C.Z.			*·6*				*0·815*	*930*	
~~Ardeer ... ...~~	~~50~~	~~42~~	~~8.~~	~~Phenyl-benzyl-urethane.~~	~~12·2~~	~~Smooth, sometimes smells of stabiliser(sweet-ish smell).~~	~~0·894~~	~~957~~	
~~Centralite type ...~~	~~50~~	~~42~~	~~8~~	~~Diphenyl-diethyl-urea and deriva-tives.~~	~~12·2~~		~~0·974~~ ~~(water liquid).~~	~~787~~ ~~(water liquid).~~	~~Cooler than M.D.~~
Gunpowder	—	—	—	—	—	—	0·726	256	—

8/20 6·5%   * Dinitrotoluene added as a moderant.

Cordite S.C.   *50*   *41*   *9*   *carbamite*   *12·2*   *Smooth*   *combined stabiliser and gelatiniser cooler than M.D.*

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 this same year (1888) cordite Mark I was recommended for use in the Service by a special committee; it was 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 the propellant very hot burning. Cordite M.D. was therefore introduced, in which a much lower percentage of nitroglycerine (30 per cent.) was employed. This has been most successful in increasing the life of guns, and it is now the principal propellant in use in the Service.

These two varieties of cordite were the chief propellants in use in the Service in 1914. Later developments will be considered in their order as they occur in the chapter.

In discussing the manufacture of the cordites and N.C.T., it is proposed to treat the manufacture of Cordite M.D. in detail, and to indicate, in the other cases, in what manner their manufacture particularly differs from that of Cordite 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. 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 oxidised to nitrogen peroxide (NO_2), which is the reddish-brown gas to which reference has been made.

Raw Materials and their Manufacture.

The principal constituents of cordite, nitroglycerine and nitro-cellulose are dealt with in detail in Chapters XI and XII. The stabilisers and solvents remain, and will now be considered.

Stabilisers.

(i) *Mineral Jelly.*—This substance is incorporated in the first four cordites mentioned in Table 13.A. It was originally introduced into cordite, Mark I, as a lubricant, but was afterwards found to possess stabilising 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*
$$\begin{array}{c} C_6H_5 \\ \end{array} \Big\rangle NH.$$
$$C_6H_5$$
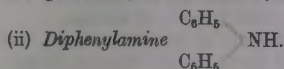
This substance is used as a stabiliser in ballistite and N.C.T. It is a crystalline substance having a melting point of 54° C. and a boiling point of 302° C. It is insoluble in water, but is readily dissolved in alcohol and ether.

(iii) ~~P.B.U. (phenyl-benzyl-urethane).~~
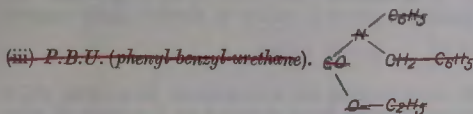
~~This is the stabiliser used in Ardeer Cordite. It is a pale brown viscous liquid at ordinary temperatures.~~

(iv) *Centralite.* (*diphenyl-diethyl-urea*).
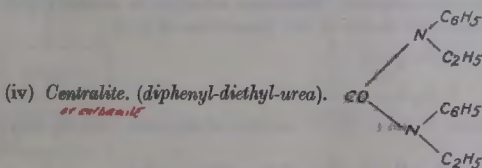
This is a white crystalline solid used in the manufacture of solventless cordite as a stabiliser and to assist gelatinisation.

Several derivatives of urea have been suggested and used as stabilisers, particularly in Germany.

Solvents.

There are two solvents used in the manufacture of cordite : *Acetone*, which is used for those cordites made from insoluble nitro-cellulose, and *ether alcohol* for gelatinising soluble nitrocellulose.

Acetone.
$$\begin{array}{c} CH_3 \\ \end{array} \Big\rangle CO$$
$$CH_3$$
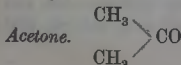
There are two chief methods by which acetone is prepared : (i) From calcium acetate, and (ii) by fermentation of vegetable matter.

(i) Acetone from calcium acetate.

$$\begin{array}{c} CH_3COO \\ \end{array} \Big\rangle Ca \xrightarrow[300°C.]{\text{Heat}} CaCO_3 + \begin{array}{c} CH_3 \\ \end{array} \Big\rangle CO$$
$$CH_3COO \qquad\qquad\qquad CH_3$$
Calcium acetate.   Acetone.
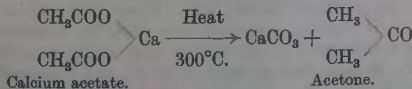
Calcium acetate is made by treating lime with acetic acid, the latter being a product of the destructive distillation of wood.

(ii) By the fermentation of starch.

Starch can be fermented to produce fusel oil, and acetone ; 100 parts of potato will, on fermentation, yield 14 parts of 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, which yielded a mixture of butyl alcohol and acetone.

Acetone is a colourless volatile liquid, possessing a characteristic odour. It has a boiling point of $56 \cdot 1^\circ$ C., and has a specific gravity of $\cdot 800$ at 15° C. It is miscible with water in all proportions. Its importance in explosives lies in its ability to dissolve highly nitrated nitrocellulose.

Ether-alcohol.

The soluble nitrocelluloses are distinguished from those which are termed insoluble by their being dissolved by a mixture of ether and alcohol ; di-ethyl ether and ethyl alcohol being those used in practice. Ether or alcohol *alone* have practically no solvent effect on these soluble nitrocelluloses. Maximum solubility is obtained with a mixture of ether and alcohol in the proportions of $3 : 2$.

(a) Ether. $\begin{array}{c} C_2H_5 \\ \\ C_2H_5 \end{array} \Big\rangle O$
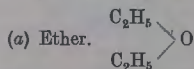
This substance is made by the action of sulphuric acid on ethyl alcohol.

(i) $C_2H_5 . OH + H_2SO_4 \longrightarrow C_2H_5 . HSO_4 + H_2O$
Ethyl Alcohol.

(ii) $C_2H_5 . HSO_4 + C_2H_5 . OH \longrightarrow \begin{array}{c} C_2H_5 \\ \\ C_2H_5 \end{array} \Big\rangle O + H_2SO_4.$
Diethyl-ether.
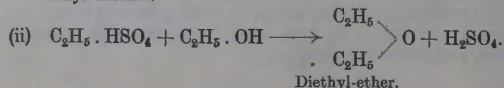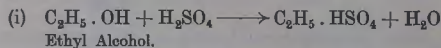
Crude ether results, together with a certain amount of alcohol, water and a little sulphurous acid. The ether is then purified by distillation.

Pure ether is a colourless, neutral and very volatile liquid boiling at $35 \cdot 6^\circ$ C. It possesses a well-known characteristic odour. Its specific gravity is $\cdot 725$ at 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. $(C_2H_5 . OH)$.

Alcohol is procured in the pure state by the distillation and subsequent drying of the crude spirit obtained by the fermentation of many kinds of vegetable matter containing sugars and starches, *e.g.*, cane or grape sugar, barley, 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 has a boiling point of 78° C., and burns with a pale non-luminous flame. It mixes with water in all proportions and forms a eutectic containing 4.41 per cent. of water. It is a useful organic solvent.

FLOW DIAGRAM FOR MANUFACTURE OF CORDITE M.D.

Wet G/C.

I week at
70°C. → 35°C.   Drying Stoves.   ← Hot Air.

Dry G/C.

Paste Mixing.   ← N/G.

Paste.

Acetone.   →   Incorporator.   ← Acetone & M.J.

Acetone
Recovery
Plant.

Dough.

Press.

Cordite.

Acetone Vapour
and Air.   ←   Acetone Recovery
Stove.   ← Heated by
Steam pipes.

Samples for
Volatile Matter   ←   Drying Stoves.
Test.

Blending.

Lotting or Gauging.

Store - Magazine.
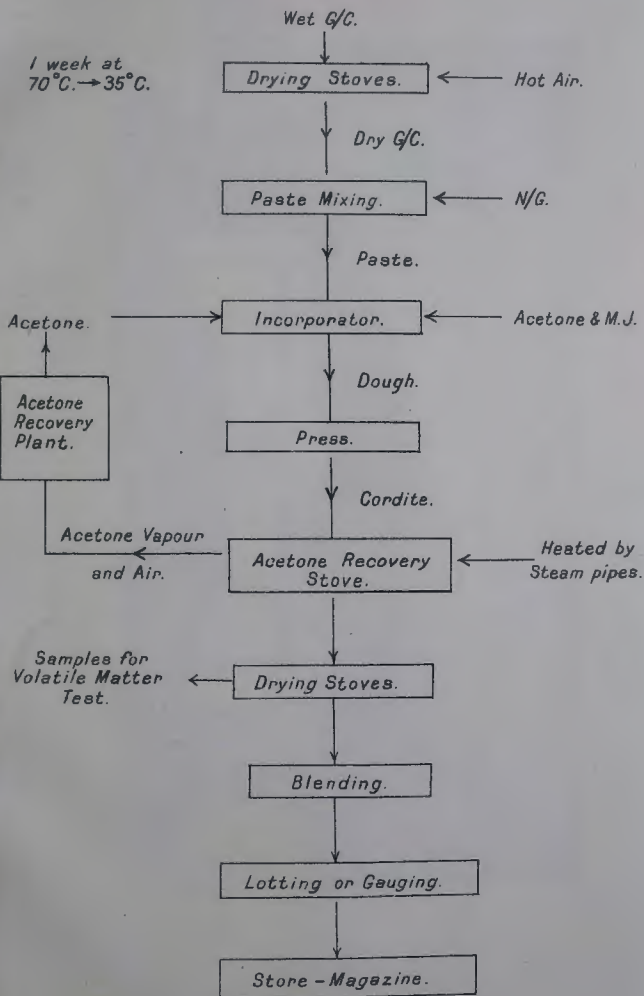
FIG. 13·1.

Fig. 13.2.
Cordite Paste Mixing Trough.
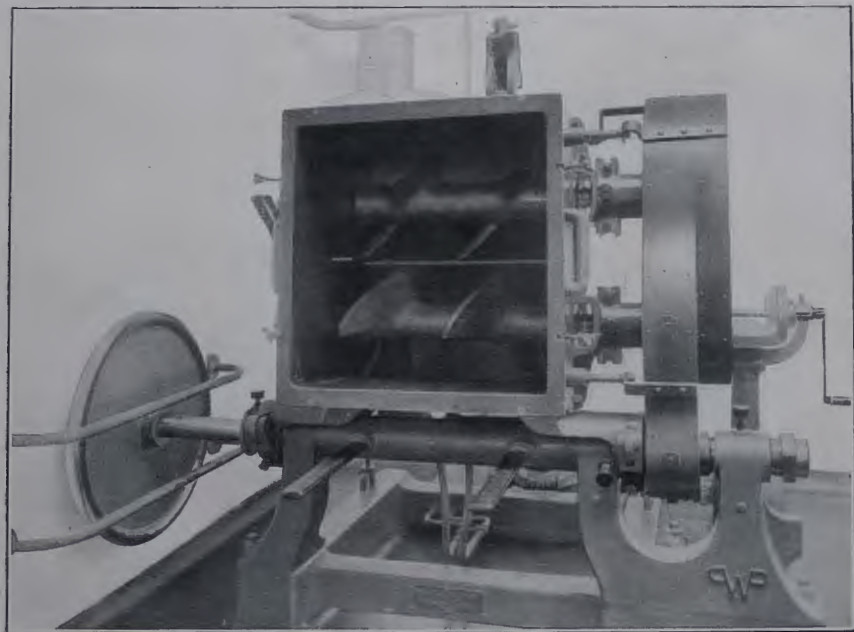
Fig. 13.3.

Incorporator. (Cordite Manufacture.)

In tilted up position.

The Manufacture of Cordite M.D.

Fig. 13.1 gives a flow diagram of the process.

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 galvanised 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.

2. *Paste Mixing.*—The dry nitrocellulose, which contains not more than 5 per cent. moisture, 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. This charge, after the addition of a measured amount of nitroglycerine, is emptied on to the mixing-table (Fig. 13.2); a pear shaped lead table having a depression at one end. The mixture is worked by hand, on the table, and through a sieve of half-inch holes formed at the bottom of the depression into a bag attached below. The product is known as " paste."

3. *Incorporation.*—The " paste " is conveyed to the Incorporation House on canvas-covered aluminium bogies. The incorporator (Fig. 13.3) is similar to the dough mixer of a machine bakery. 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. The machine is run for three hours ; at the end of that period the appropriate quantity of mineral jelly is added. Incorporation is then continued for another three hours, when the " dough," as it is now called, is ready for the next process.

4. *Pressing.*—In this operation the " dough " is pressed, through a die, emerging in the familar cord form of cordite. This is accomplished in a hydraulic press (Fig. 13.4), 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.

5. *Cutting or Reeling.*—(a) In the case of the larger sizes (4¼ and upwards), 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, such as are used for rifle cartridges, 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.

$$CH_3 \diagdown \quad \diagup OH$$
$$C$$
$$CH_3 \diagup \quad \diagdown SO_3Na$$
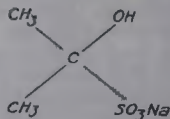
(ii) From this salt the acetone is recovered by distillation with a solution of sodium carbonate.

$$2(CH_3)_2-C\diagup^{OH}_{SO_2Na} + Na_2CO_3 \longrightarrow 2Na_2SO_3 + CO_2 + H_2O + 2(CH_3)_2CO$$
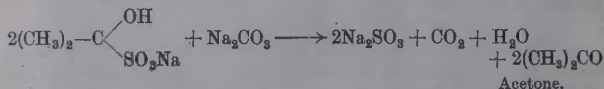
Acetone.

(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 varied slightly according to the size of cordite to be dried; the smaller sizes requiring a lower temperature than the larger. Thus the reels of rifle cordite require only a few days at 15–20° C. In most cases, however, the temperature is maintained at about 40° C. The time of drying varies with the size of the cordite.

Thus : Size 45 requires 37 days.
,, 19 ,, 14 ,,
,, 4¼ ,, 7 ,,

Towards the end of the period samples are taken for the specification test for volatile matter.
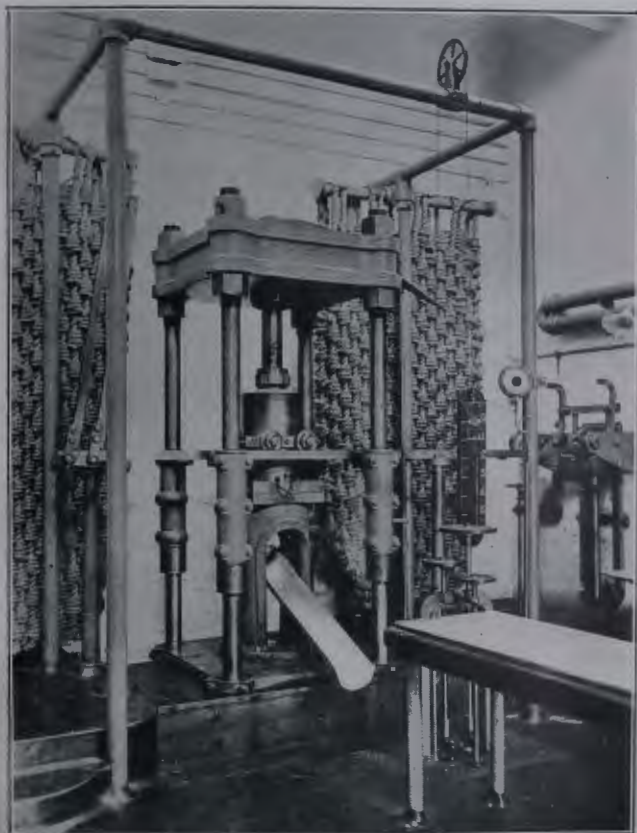
FIG. 13.4.—Cordite Press.
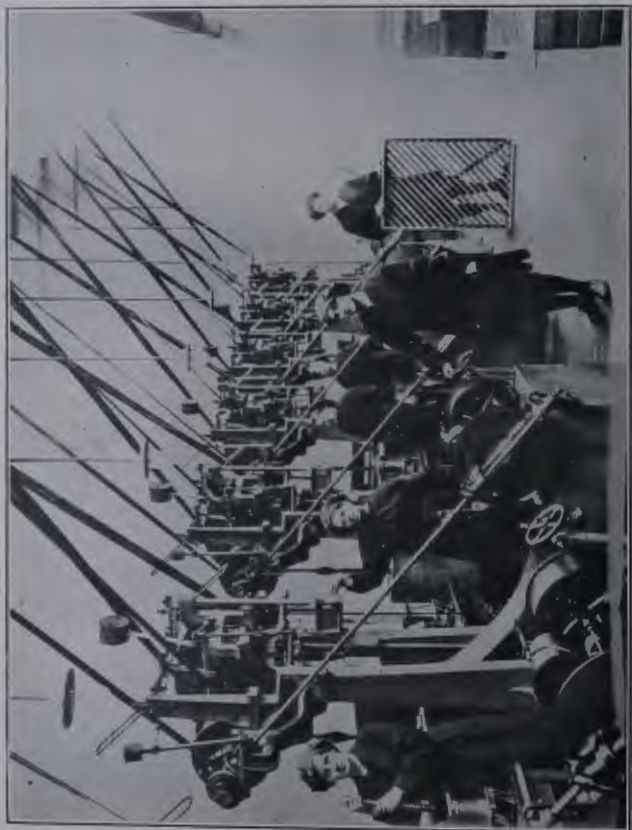
FIG. 13.5.—Rifle Cordite Presses.

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.

9A. *Lotting.*—Blends are further mixed into lots, eight blends forming a lot. These blends 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 been introduced lately in place of 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. 13.6.

At present this is a manual operation but it is probable that gauging will be performed mechanically in the near future.

The machine 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
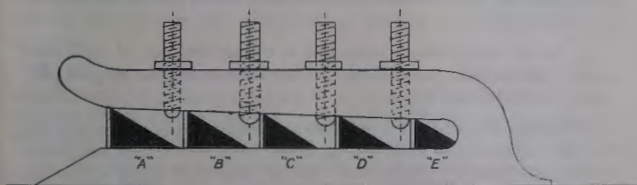
FIG. 13.6.—Machine for Gauging Cordite.

cord, decreasing progressively from left to right. The operator slides a stick between the jaws of the gauge, and along, until the stick encounters a micrometer which will not allow it to pass. 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."

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."

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 cordite M.D. applies also to the manufacture of cordite Mark I and cordite M.C. Cordite R.D.B. and the "solventless" cordites are treated somewhat differently.

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 13.A shows that cordite R.D.B. differs from cordites Mark I, M.D., and M.C. in the employment of nitrocellulose containing only 12·2 per cent. nitrogen. This is a "soluble" nitrocellulose, and therefore ether-alcohol 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. *Alcohol Dehydration.*—Instead of air-drying the wet nitrocellulose, the water is displaced from it by alcohol under pressure. The alcohol is not removed from the nitrocellulose as it forms part of the solvent at a later stage.

2. 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.

3. *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.

4. The final stove drying is much quicker than in the case just considered. 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 and costly to maintain. 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 the cordite is also appreciably affected by its maintenance at a comparatively high temperature (circ. 40° C.) for several days.

To overcome these difficulties, the " solventless " process has been designed. The principles employed are not very different from those underlying the manufacture of ballistite. That is to say, the gelatinisation 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 stabiliser in the finished propellant, serves during manufacture to enhance the gelatinising action of the nitroglycerine. A brief mention of some of these substances will be found earlier in this chapter.

The name " *solventless* " cordite is, therefore, somewhat misleading ; the characteristic feature of these propellants being the employment of a *non-volatile solvent.*

Manufacture of " Solventless " Cordite.

1. The nitrocellulose is pulped to a finer state of division than is usual, and the excess of moisture is pressed out.

2. The nitrocellulose, nitroglycerine, and gelatiniser are mixed under water, agitation of the mixture by compressed air being employed. During this process the nitrocellulose absorbs the other two constituents.

3. The excess of water is removed by draining and pressing. The moisture is then reduced to about 5 per cent. by passing the mixture between slowly moving, heated rollers. Final drying is accomplished by a short stoving at 49° C.

4. The dried material is then readily gelatinised by passing it a few times between heated rollers, the mixture now taking the form of sheet cordite.

5. The sheet is stamped into discs, and, after a preliminary heating, the discs are loaded into the heated cylinder of the press.

6. Extrusion into the final cord form follows, after which the cordite is ready for use.

The time occupied 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. For the same reason, the cordite cannot be forced through strainers during the operation of pressing. 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.

(B 28/231)z   H

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 serious disadvantage of " solventless " cordite is the impossibility of straining it during pressing. It is therefore difficult to avoid the inclusion of small particles of foreign matter which may cause corrosion.

PROPERTIES OF CORDITE.

Cordite is a " colloid," *i.e.*, it has no internal structural form. 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. Therefore control of the rate of burning can readily be exercised by varying the size or shape of cord.

It is a translucent substance, varying in colour from light to dark brown.

When in good condition it has very little smell ; when decomposition is advanced a distinct smell of the oxides of nitrogen is noticeable. In the case of the " solventless " cordites, the characteristic odour of the stabiliser is sometimes apparent.

Finely ground cordite ignites at about 152° C. Ignited in the open in small quantities it burns furiously, 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 nitroglycerine. It is not appreciably affected by damp. Direct sunlight will cause rapid 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.—70 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 breech 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. and M.C., or 45° F. for Mark I and R.D.B. Prolonged storage under these conditions may affect
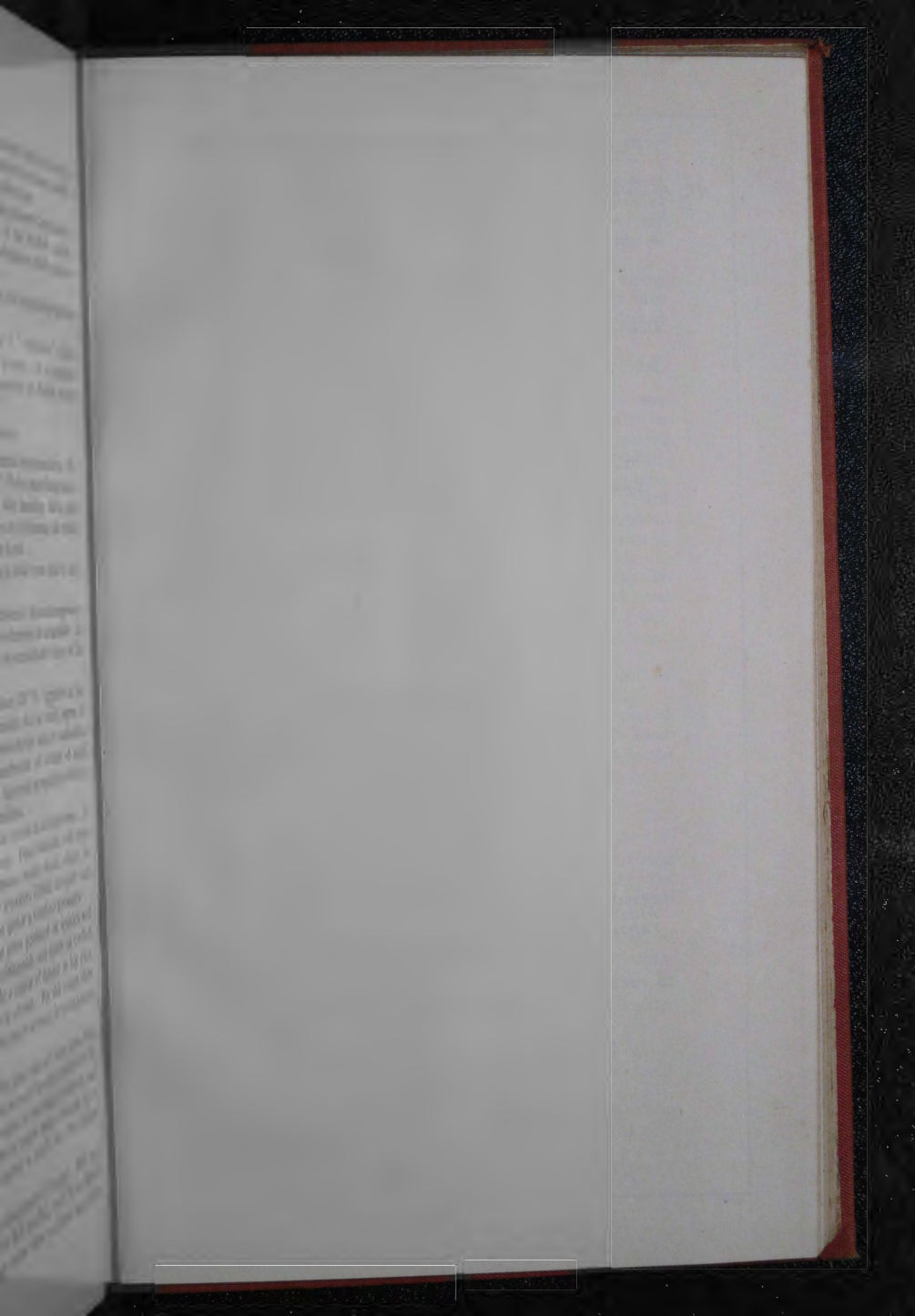
FLOW DIAGRAM FOR MANUFACTURE OF N.C.T.

N/C Propellants

↓ Wet N/C

Alcohol → ☐ **Dehydration Press** → Water

↓ N/C + Alcohol

Ether →
Diphenylamine → ☐ **Incorporator**

↓ N/C Dough + 0.5% Diphenylamine

☐ **Press**

↓ N/C Tubes
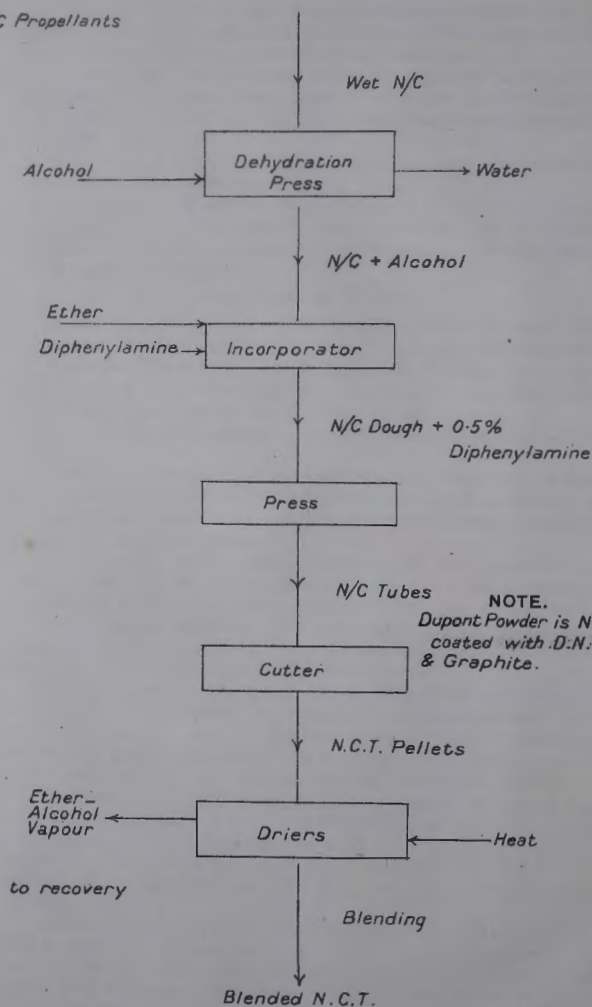
NOTE.
Dupont Powder is N.C. coated with D:N:T: & Graphite.

☐ **Cutter**

↓ N.C.T. Pellets

Ether–
Alcohol ← ☐ **Driers** ← Heat
Vapour

to recovery

↓ Blending

Blended N.C.T.

N.C. = Nitrocellulose.
D.N.T. = Dinitrotoluene.

FIG. 13.7

1507

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 is then ignited, any nitroglycerine absorbed by the paper will be evidenced by a green edge to the flame.

(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 conductivity about equal to that of porcelain. To retard the rate of decomposition of cordite, substances (stabilisers) are added to it, which combine with the free acids to form innocuous products, and so stabilise 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. 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, with the production of unstable lower nitrates. Non-absorbent paper is therefore used to line all boxes containing cordite.

Nitrocellulose Tubular. (N.C.T.)

This is the standard propellant in U.S.A., and large quantities were imported from that country for use in the Service during the Great War. Its manufacture was also developed to a small extent in this country.

Fig. 13.7 is a flow-diagram showing the 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 therefore there is no paste mixing. Alcohol dehydration is employed.

2. ·5 per cent. of diphenylamine is used as a stabiliser in two of the varieties of N.C.T., viz., that manufactured in this country and that made by the Dupont Company in U.S.A.

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 powdery friable mass, and must be compressed in order to bring it into a compact form.

    (b) The nitrocellulose is then filtered by forcing it through a wire gauze strainer under pressure.

    (c) The filtering operation breaks up the nitrocellulose once more, and a further compression is needed to regain the compact condition.

    (d) Finally, the nitrocellulose 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 or 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 60-pdr.

Properties of N.C.T.

N.C.T. is lighter in colour, and is not so well gelatinised as cordite, and it therefore exhibits a capacity for absorbing moisture. This does not affect its properties as an explosive, but it alters the loading density and so leads to irregular pressures and inaccurate shooting. It 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 nitrocellulose is gelatinised by nitroglycerine, and not by a volatile solvent.

FLOW DIAGRAM FOR MANUFACTURE OF BALLISTITE.

↓Wet N/C pulp. (12·6 + 13·2)

N/G. ——→
Air stirring. ——→ | Mixing Cylinder. | ←— Warm water.

↓

| Drainer. | ——→ Water + trace N/C.

Wet (N/C + N/G)

↓

| .Press. | ——→Water.

↓

| Cutter. |

Blended.

↓

Ballistite Squares.

N/C = "Nitrocellulose"
N/G = "Nitroglycerine."

FIG. 13·8

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 powdery friable mass, and must be compressed in order to bring it into a compact form.

    (b) The nitrocellulose is then filtered by forcing it through a wire gauze strainer under pressure.

    (c) The filtering operation breaks up the nitrocellulose once more, and a further compression is needed to regain the compact condition.

    (d) Finally, the nitrocellulose 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 or 5 months at 44° C. is quite usual.

N.C.T. is known in its various sizes by its diameter in hundredths

"This moisture does not prevent it function-ing as an explosive, but causes variation in ballistics which leads to inaccurate shooting, and is due to the heat absorbed by the volatilisation and dissociation of the water present, and the consequent effect on the rate of burning. The ease of ignition is also affected, particularly if the powder grains are externally wet."

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.

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FLOW DIAGRAM FOR MANUFACTURE OF BALLISTITE.

Wet N/C pulp. (12·8 + 13·2)

N/G. ──────────┐
Air stirring ──────► | Mixing Cylinder. | ── Warm water.

| Drainer. | ── Water + trace N/G.

Wet (N/C + N/G)

| Press. | ── Water.

Steam. ──────► | Drying Rolls | ── Water.

Dry (N/C + N/G) ungelatinised
(2% aq.)

Steam ──────► | Incorporating rolls. |

do. gelatinised.

| Cutter. |

Blended.

Ballistite Squares.
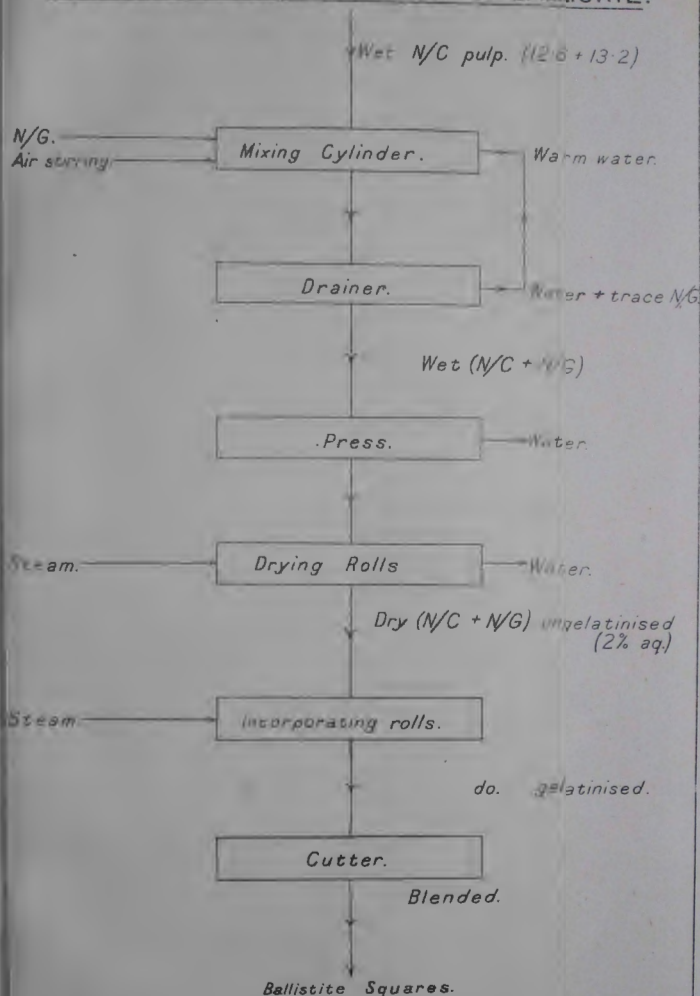
N/C = "Nitrocellulose"
N/G = "Nitroglycerine."

FIG. 13·8

FIG. 13.9.

Ballistic Apparatus, &c.

Ballistite has the following composition :—

	Per cent.
Nitroglycerine	.. 39·5
Soluble nitrocellulose	.. 60·5

Manufacture.

Fig. 13.8 is a flow-diagram of the present method of making ballistite.

1. The nitrocellulose in the form of a wet pulp is agitated with the correct amount of nitroglycerine by compressed air, in the presence of a large excess of water. The nitroglycerine is absorbed by the nitrocellulose, 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 nitroglycerine and nitrocellulose between hot rollers. The dry ungelatinised 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. 13.9).

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 gelatinised 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 gelatinised. 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 howitzers, small guns and mortars. 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 is added to it as a stabiliser, and other substances such as camphor, calcium carbonate and aniline have been tried in the past for that purpose, 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.

<div align="center">

Chapter XIV.

THE RECOVERY OF WASTE ACIDS.

</div>

Introduction.

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 many of the nitrating processes discussed in the previous chapters, whether it has been the nitration of toluene to trinitrotoluene or the nitration of glycerine to nitroglycerine, a mixed acid consisting of nitric acid, sulphuric acid and water in various proportions has invariably been employed.

During nitration a considerable amount of the nitric acid is used up, with the formation of an equivalent amount of water. The resulting waste acid therefore differs from the original mixed acid in two ways : (i) it contains a greatly-reduced percentage of nitric acid, and (ii) the percentage of water present has been increased. The amount of sulphuric acid remains very nearly constant, a little being lost in the side reactions that inevitably accompany nitration.

To emphasise this point the following approximate figures for the nitration M.N.T. to T.N.T. are quoted :—

					Mixed Acid. Per cent.	Waste Acid. Per cent.
H_2SO_4	..	..	..	..	80	72
HNO_3	..	..	..	..	18	3
H_2O ..	..	..	..	..	2	25

The general reaction of nitration may be symbolised by the two equations given below. The first represents the nitration of benzene derivatives such as phenol, toluene, &c. The second equation is that for the nitration of bodies such as cellulose and glycerine. In both cases water is formed as a product of the reaction.

1. $R|H \quad + \quad HO|NO_2 \longrightarrow RNO_2 + H_2O$

2. $R|OH \quad + \quad H|ONO_2 \longrightarrow RONO_2 + H_2O$
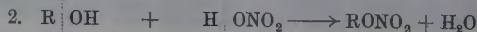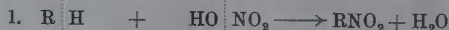
The manner in which the recovered acids enter into the general scheme for the circulation of acids in any explosives factory is illustrated by Fig. 14.1. It is obvious from the foregoing that the waste acids are of considerable value in so far as they can be recovered in a form suitable for further use.

FLOW OF ACIDS IN AN EXPLOSIVES FACTORY.

Pyrites.

Sodium Nitrate.

Sulphuric Acid Plant.

Nitric Acid Plant.

Sulphuric Acid.

Sulphuric Acid.

Nitric Acid.

Cotton Cellulose Glycerine Phenol Toluene etc.

Sulphuric Acid Storage.

Nitric Acid Storage.

Sulphuric Acid.

Nitric Acid.

Sulphuric Acid.

Acid Mixing.

Mixed Acid.

Nitrator.

Nitric Acid.

Waste Acid.

Sulphuric Acid Concentrators.

Sulphuric Acid.

Denitration Plant.

FIG. 14·1.

HIGH TEMPERATURE DENITRATING COLUMN.

116° C.

Waste Acid.

Fume Main.

Cooling Coils.

Pottery

To Flue 430° C.

Cast Iron

Packed Graded Quartz

Still Watcher

To Nitric Receivers

HNO_3 90%
HNO_2 2·5%

Denitrated acid 75% H_2SO_4.
175° C.

from cooler at 15° C.

Lead Cooler
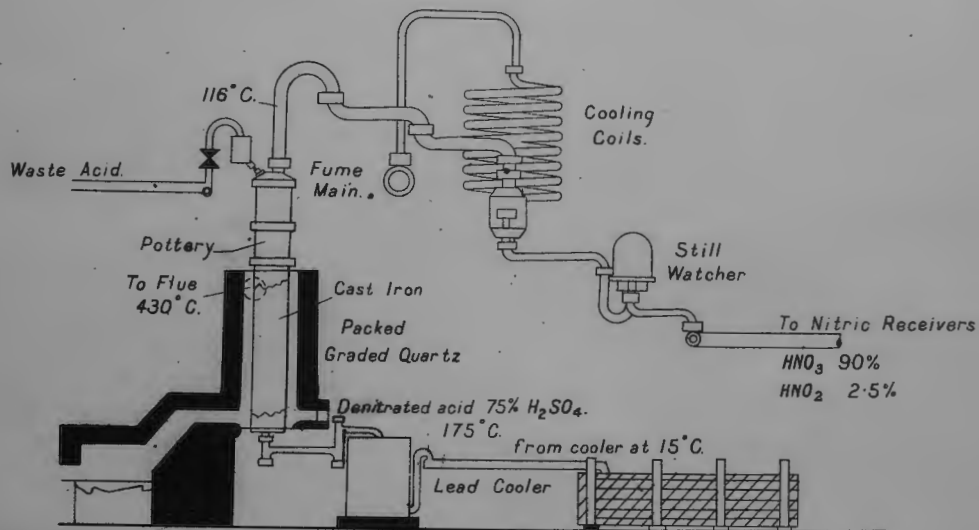
FIG. 14·2

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

> (i) To use the waste acids as collected, for some other operation for which they may be suitable (*cf.* p. 54).
> (ii) To add fresh strong acids to the waste acids, until the final product has the required composition. This requires no further elaboration.
> (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 the present chapter.

This separation of the nitric acid from the sulphuric acid is 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.

(*b*) Column Denitrators (Fig. 14.2).—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. Superheated steam is used as the source of heat.
> (ii) High-temperature columns are made of acid resistant cast-iron, and are heated externally by hot furnace gases.
3. Condensers and absorption towers.

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

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

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

$$H_2O + 2NO_2 \longrightarrow HNO_2 + HNO_3$$

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 not readily decomposed by superheated 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.

    (*b*) Cascade concentrators :

        These are inefficient, and are expensive to maintain and are now obsolete.

    (*c*) Tower concentrators :

      (i) Gaillard Towers.

      (ii) Gilchrist Towers.

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

(*a*) *Kessler Concentrator* (Fig. 14.3, (*a*) and (*b*)).—This consists of a small tower of acid-proof brickwork, in which trays of the type shown in the diagram 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.

(*b*) *Cascade Concentrators.*—The acid is fed into the top of a long series of pans arranged on a slope, so that the acid traverses

URIC ACID

TOR.

3A.
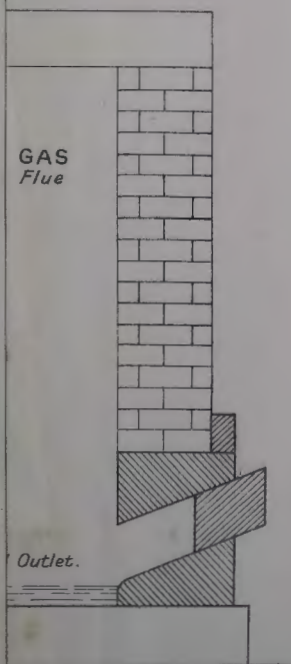
GAS
Flue

Outlet.

Acid Inlet

Gas

Gas

Gas

Gas

Gas

Gas
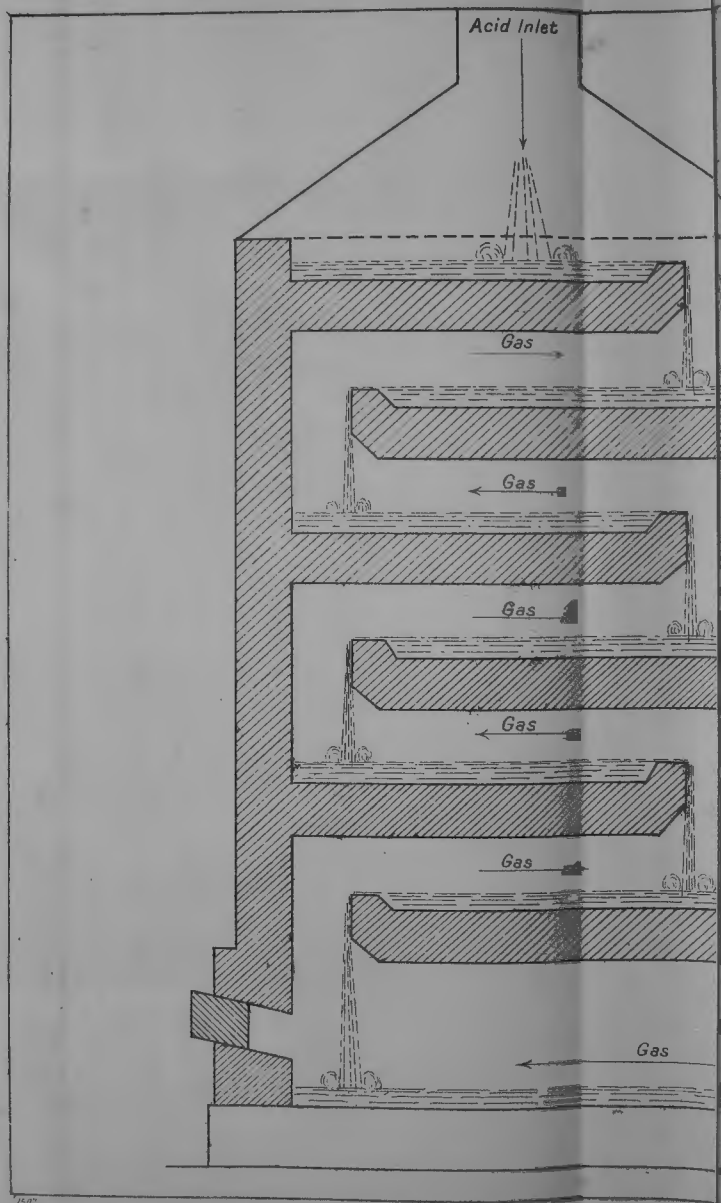
15.0"

Fig. 14.3 (*b*).—Kessler Concentrators.

GAILLARD CONCENTRATORS.

DIAGRAM SHEWING PATH OF GASES FROM COMBUSTION CHAMBER TO STACK.

Stack

Feed 69·3%

Recuperator

Tower

Gas B.T.U. 128·5
CO_2 5·4
CO 22·2
CO_4 18
H_2 12·4

Precipitator

Scrubber

Fan

Combustion
Chamber

Fan
16 in. 1260 R.P.M.

Mud Box   Cooler   Gas
Flues
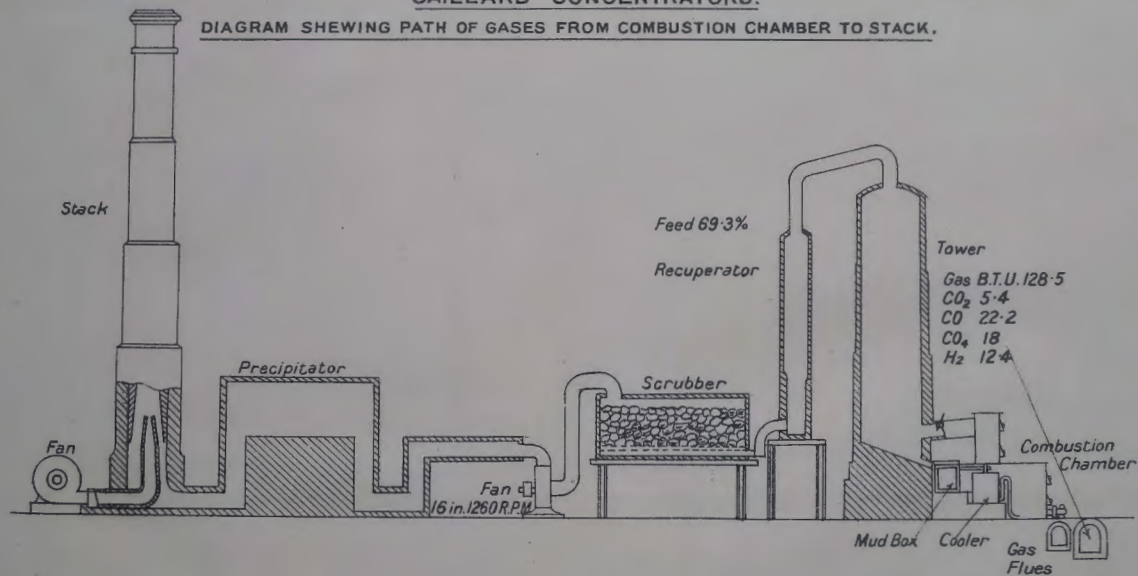
FIG 14.5

the whole series of pans by overflowing from one pan into the next below it.

The pans in the first third of the run are made of lead, and in these the acid is heated prior to its concentration in the lower pans. The latter are made of fused silica or silicon-iron, and are covered with a hood from which fume mains are led, for the removal of the acid fumes produced as concentration proceeds. The whole series of pans is heated by hot furnace gases, which ascend a flue situated underneath the pans.

By the time the acid has reached the bottom of the cascade, it is sufficiently concentrated to be cooled and stored.

(c)—(i) *The Gaillard Tower.*—The acid is sprayed down a tower against a flow of hot furnace gases. The concentrated acid is collected at the bottom of the tower, cooled, and stored.

(ii) *The Gilchrist Tower.*—The acid undergoes a preliminary concentration in a tower packed with acid-proof bricks. The partially concentrated acid is then collected in a long covered trough, and the action of hot furnace gases playing on the surface of the liquid completes the concentration as in the Kessler plant.

The concentrated acid produced by any of the methods just described contains 96 to 97 per cent. of sulphuric acid.

3. *Recovery of Acid Fumes.*—In all the methods of concentration outlined above, acid is carried away in the fumes, and it is important that this acid should be recovered, both in the interests of economy, and because it is undesirable that the acid fumes should escape into the outside air.

The majority of the acid can be recovered by passing the fumes through either coke scrubbers or Glover towers ; the final removal can then be carried out in the Cottrell electrostatic precipitator.

(a) In the case of coke scrubbers, the acid fumes are passed through a series of rectangular lead chambers packed with graded coke. The acid collected at the bottom of the tower can then be concentrated by any of the methods described above.

(b) In the Glover tower, the acid fumes ascend a tower packed with acid-proof brickwork against a stream of weak acid.

(c) The fumes issuing from the coke scrubbers or Glover towers contain a certain amount of acid mist, which cannot be recovered by any scrubbing process. If, however, the particles can be electrically charged, they will be attracted to a plate carrying a charge of the opposite sign, and so can be collected. This is done in the Cottrell electrostatic precipitator.

This consists of a chamber carrying the plates of a large electrical condenser, of which air is the insulating medium. The plates are charged to a pressure of some 60,000 volts, and the acid particles collect on the plates in the manner indicated above, and drain to the base of the chamber.

The general arrangement of a concentrating plant employing a Gaillard tower, coke scrubbers and a Cottrell precipitator, is shown in Fig. 14.4.

E.—CHEMICAL STABILITY OF EXPLOSIVES

CHAPTER XV.

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.

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 very small causes. 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.

As a class, high explosives are characterised 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.

Only those explosives, classed in this book as propellants, remain and these 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 XI and XII.

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). As decomposition advances, heat is generated, leading ultimately to spontaneous ignition. Many years are, of course, required before this cycle of changes is complete, but careful watch over the condition of material in the Services is necessary to ascertain that it is not approaching an unduly unstable condition.

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 136° C. consist approximately of 40 per cent. nitrogen peroxide (NO_2) and 60 per cent. nitric oxide (NO). The guncotton is oxidised 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 oxidised 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 gelatinised 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 minimised by the fact that nitroglycerine is not so readily oxidised as nitrocellulose and therefore explosives which include nitroglycerine share this advantage to a certain extent.

These actions 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 in 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 neutralise 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 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 on page 101).

Stabilisers.

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 centralite and P.B.U. (*See* Chapter XIII.)

The action of diphenylamine and the derivatives of urea may be exemplified by the reaction given below for the first mentioned.

$$\begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \end{matrix} NH + HNO_2 \longrightarrow \begin{matrix} C_6H_5 \\ \diagdown \\ C_6H_5 \end{matrix} N . NO + H_2O .$$

Diphenylamine.   Nitrous acid.
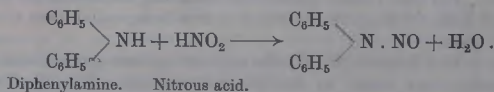
Mineral jelly acts as a stabiliser by virtue of the unsaturated hydrocarbons it contains. It also prevents atmospheric oxidation by rendering the surface of the explosive impervious. If mineral jelly is subjected to the heat treatment known as " cracking," the percentage of unsaturated hydrocarbons is increased, and its stabilising 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.

$$(C_{2n}H_{4n+2} \longrightarrow C_nH_{2n+2} + C_nH_{2n})$$
Paraffin.   Paraffin.   Olefine.
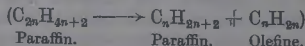
FIG. 15.1.
Apparatus for Abel's Heat Test.

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.

All 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 colouration 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.

(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. 15.1).

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 standardised conditions. The lower 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 lays down a minimum of 30 minutes at a temperature of 180° F. (82·2° C.). Cordite 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 gelatinised with ethyl acetate or alcohol, since these solvents prolong the test unduly.

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. 15.2 (*a*) and (*b*).)

This is a fume test originally introduced for the examination of Cordite, Mark I. Full details will be found in R.A.O.S., Part II.

A weighed sample of cordite which has been ground and sifted, is contained in a Dewar vacuum flask, the outer jacket of which is silvered (Fig. 15.2 (*b*)). A thermometer ((B), Fig. 15.2 (*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.

The cordite is maintained at a temperature of 80° F by immersion in a bath (D), heated by a burner (E) which is controlled by a gas regulator (C). After some time, red 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 will stand such a test for 500 or 600 hours. It is 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 is intended to imitate adverse conditions of storage.

The Vacuum Test. (Fig. 15.3 (*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
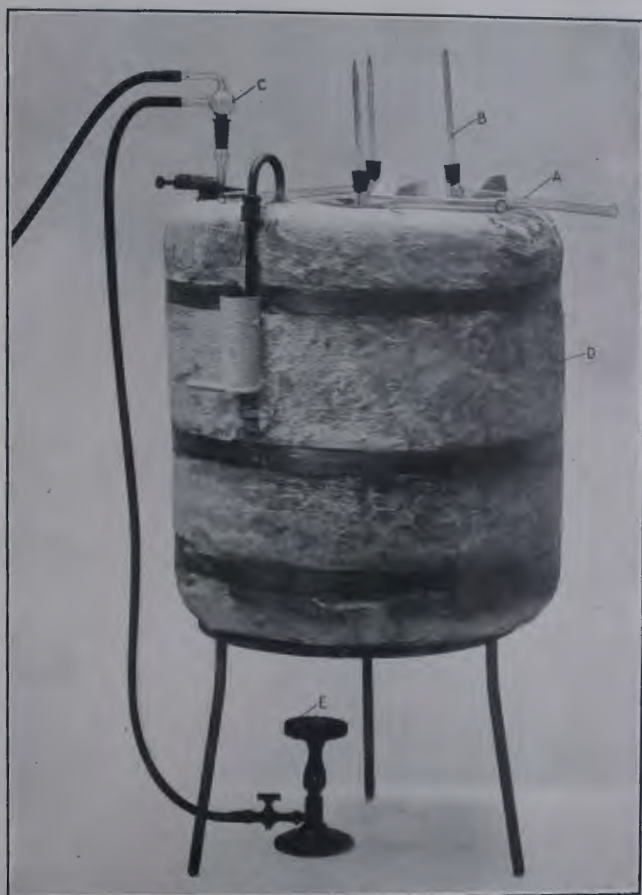
Fig. 15.2 (*a*).
Silvered Vessel Test.
General Arrangement.
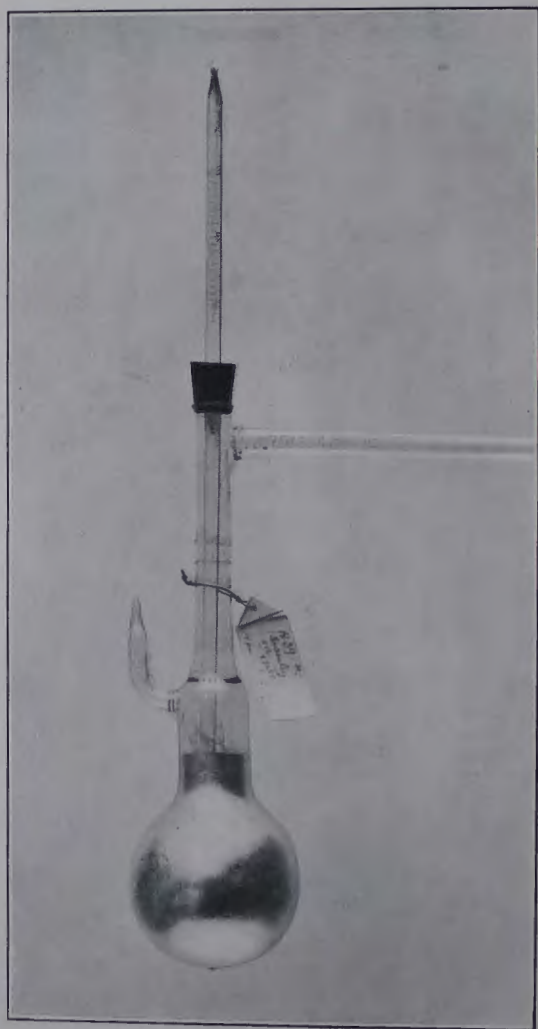
Fig. 15.2 (b).
Silvered Vessel.
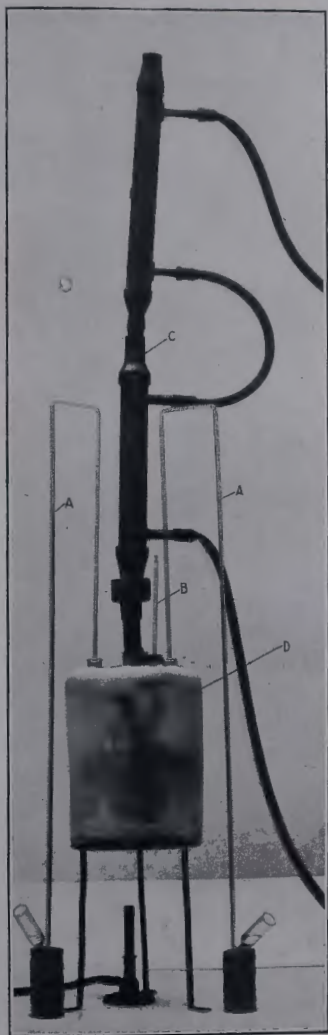
FIG. 15.3 (*a*).

Vacuum Test.

A Vacuum test in operation. The test tubes (seen at A Fig. 15.3 (*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).
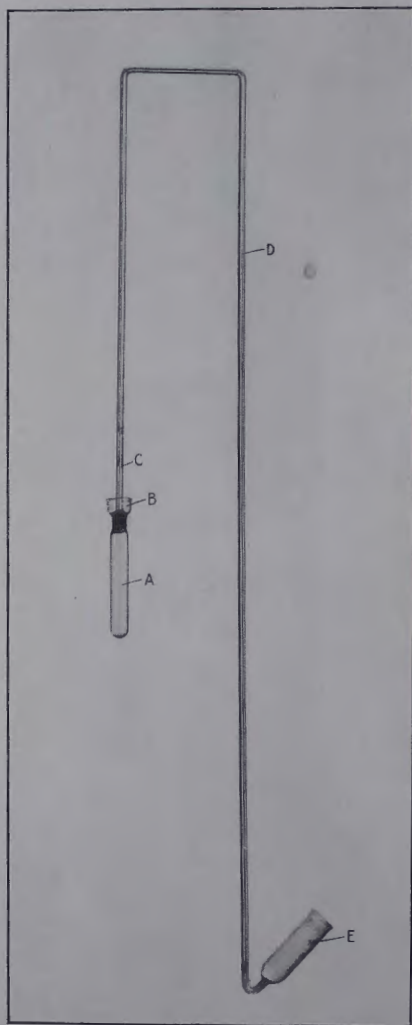
FIG. 15.3 (b).—Detail of Vacuum Tube and Manometer.

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).
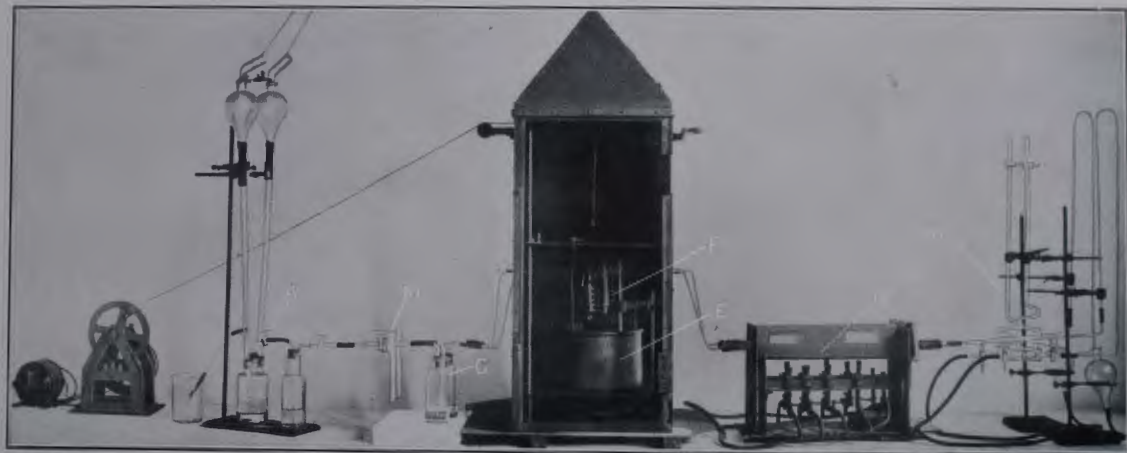
FIG. 15.4 (a).—General Arrangement of Will Test.

On the left side at (A) is the apparatus for generating Carbon Dioxide by the interaction of Hydrochloric Acid and Sodium Carbonate 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 Sodium Hydroxide.
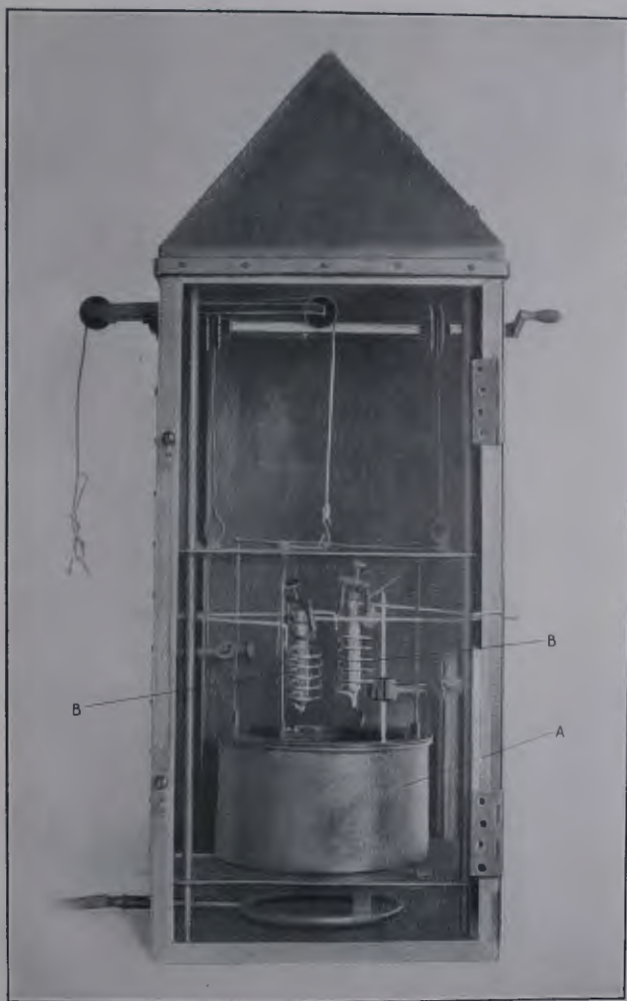
Fig. 15.4 (b).—Detail of Apparatus for Will Test.

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).
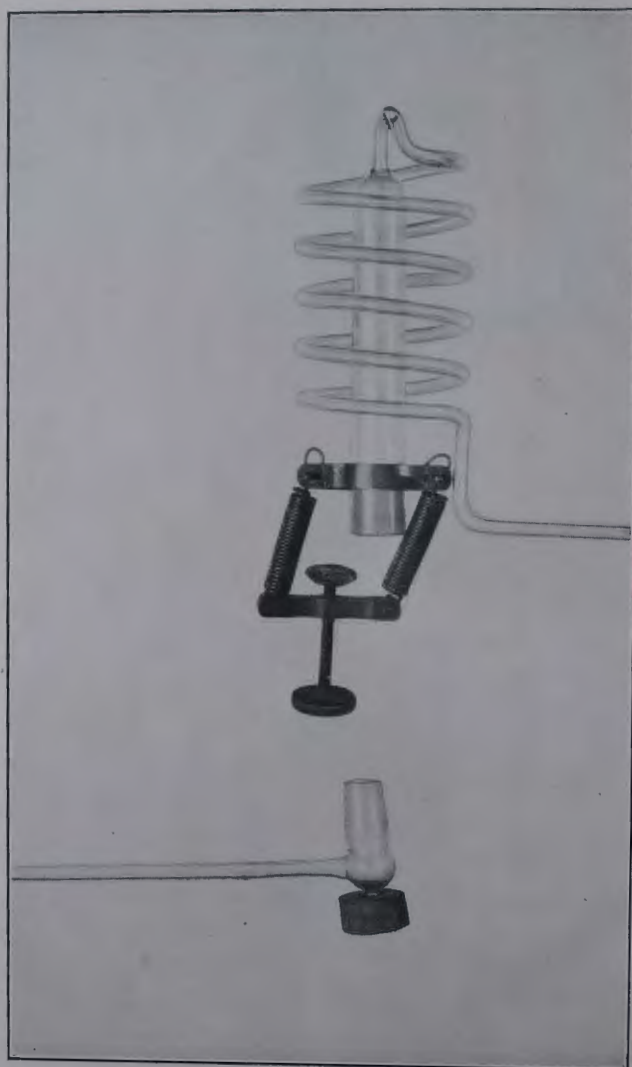
FIG. 15.4 (c).—Detail of Combustion Tube.   Will Test.

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.
4. Height of mercury in manometer.
5. Height of mercury in barometer.

The first reading is taken $1\frac{1}{2}$ 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 m.m. of mercury).

Not more than 4 c.c. (corrected) of gas should be evolved in 40 hours at 120° C.

Will Test. (Fig. 15.4 (*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 other organic gases which are evolved to carbon dioxide and water. The volume of nitrogen so obtained is measured in a gas burette filled with sodium hydroxide solution in which carbon dioxide is readily absorbed.

$2 \cdot 5$ grams of good service guncotton will yield $6 \cdot 5$ to $8 \cdot 5$ milligrams of nitrogen in four hours (*Robertson*).

Bergmann and Junk's Test.

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 a glass tube ; three tubes are prepared, one being used as a blank.

The two test tubes (A, A), after being fitted with absorption bulbs (B, B) containing 30 to 40 c.c.s. 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. 15.5 (*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.s. 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.s. 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.s. 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 temperatures of storage is that of fuze 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.

F.—INITIATORS.

Chapter XVI.

MERCURIC FULMINATE, CAP COMPOSITIONS, LEAD AZIDE.

Mercuric Fulminate. $Hg \ (OCN)_2$.

Introduction.

This is the mercuric salt of fulminic acid.   The latter has not yet been isolated, and its exact chemical constitution is still a matter of some uncertainty.   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 :—

$$Hg \ (OCN)_2 \longrightarrow Hg + 2CO + N_2$$
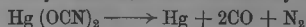
This breaking up is accompanied by a great evolution of heat.   This is due in part to the heat of decomposition of the fulminate, and in part to the exothermic oxidation of the carbon to carbon monoxide.
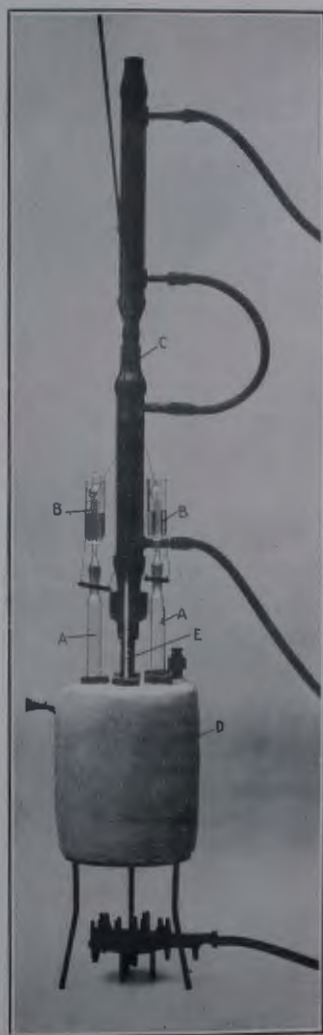
FIG. 15.5 (a).
Bergmann and Junk Test.
General Arrangement.
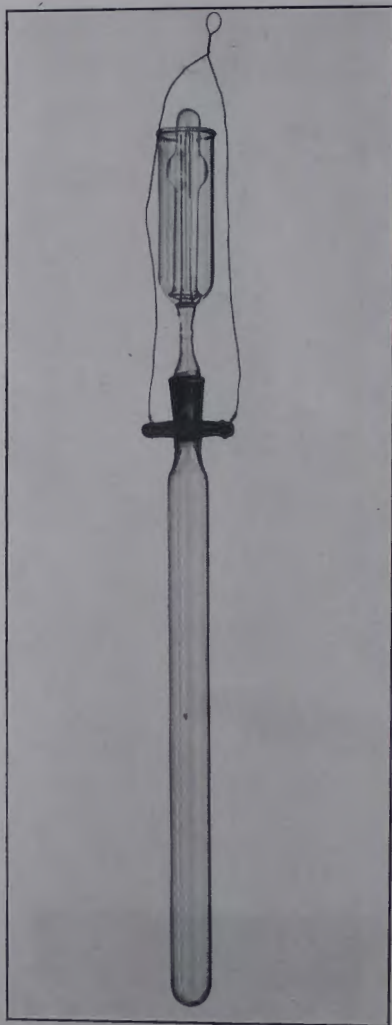
FIG. 15.5 (b).—Test Tube and Absorption Bulbs for Bergmann and Junk Test.

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 25° 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 $\frac{1}{2}$ 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.

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 flame, a blow, or an electrically heated wire, as the case may be.

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 these means 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 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 16.A.

| | S.A. Percussion caps. | | Cap in German T. & P. Fuze. | Friction tube. | Detonating Composition " A " Mixture. |
	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.

Potassium chlorate when used in S.A. caps 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 extraneous gritty matter. The materials are mixed dry, by gentle agitation in a conical fabric 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. They are usually prepared by indirect methods. Lead azide has an advantage over other metallic azides in its ease of preparation.

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 :

$$N_2H_4 + C_2H_5NO_2 + NaOH \longrightarrow NaN_3 + C_2H_5OH + 2H_2O$$

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 equally sensitive whether it is wet or dry, and

is not rendered safe by immersion in water; 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. At ordinary temperatures, carbon dioxide in the presence of moisture liberates hydrazoic acid, which may attack the copper case of detonators.

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 more sensitive to friction than mercuric fulminate, but is 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 may be used to replace mercuric fulminate in detonators and similar devices.

G.—MISCELLANEOUS COMPOSITIONS.

CHAPTER XVII.

ILLUMINATING, SIGNAL, SMOKE AND INCENDIARY COMPOSITIONS.

Those compositions mentioned in the third main category of the Service Classification of Explosives in Chapter II, alone remain to be considered.

ILLUMINATING AND SIGNAL COMPOSITIONS.

These differ from explosives in that they are intended to burn slowly, regularly, and without violence, from an exposed surface. The ingredients are generally finely ground and mixed, and finally brought to a dense state, by compression, or by incorporation with some organic combustible binding material such as paraffin wax or shellac varnish. Wax, if used, reduces sensitiveness to shock or friction, helps to waterproof the material, and protects such ingredients as powdered metals from oxidation, besides helping to regulate the speed of burning. Most of these compositions are more sensitive than ordinary high explosives, and are readily ignited by spark or flame ; they usually require protection from moisture.

The basis of most miscellaneous compositions is a readily combustible material mixed with a solid oxygen-bearing compound. Other ingredients are used to regulate the speed of burning, to give colours to the light produced, to reduce sensitiveness, or to bind the ingredients into a convenient solid form.

When an intense illumination is required, powdered magnesium, aluminium, or a mixture of both these metals, is employed, the oxygen-bearing substance usually being potassium chlorate or nitrate. Other chlorates or nitrates may also be used.

For purely signalling purposes, where a very intense light is not necessary, the powdered metals may be replaced by combustible organic material such as charcoal or shellac. These, mixed with suitable oxidising agents, burn brightly, and are used for the signal lights discharged from the Very pistol. All mixtures of chlorates and combustible material are sensitive to friction, this being particularly the case if powdered magnesium is also present.

The addition of salts of certain metals imparts a characteristic colour to the light produced on burning. Salts of sodium produce an intense yellow colour, which can be changed to white by the further addition of a salt of lead, or of powdered metallic antimony. Barium salts give green light ; strontium salts, red ; whilst basic copper carbonate gives a blue colouration. Mercurous chloride (calomel) decreases the rate of burning, and increases the brilliancy of the light

produced. Sugar of milk (lactose), and wood meal are sometimes used to provide a suitable combustible material. Sulphur is also occasionally employed as an ingredient ; it lowers the ignition point.

These compositions may be used in a variety of forms. As flares they may be burnt on the ground, in holders, or suspended from a suitable support. As stars, they may be discharged from a Very pistol, from a rocket, or from a star shell. In the latter case they are generally attached to a parachute. Illuminating compositions are also used for filling night tracers for shells. Precautions must be taken to avoid the development of pressure which would tend to make the composition explode ; the products of combustion must be allowed to escape freely, and the burning surface prevented from becoming choked with slag.

The following exemplify various types of composition, the numbers representing parts by weight.

GROUND FLARES.

White.		*Red.*	
Potassium chlorate .. 64		Strontium nitrate 60	
Potassium nitrate .. 14		Potassium chlorate .. 2	
Antimony powder .. 14		Calomel 3	
Charcoal 4		Shellac 3	
Shellac 4			

Yellow.		*Green.*	
Sodium nitrate 70		Barium nitrate 55	
Shellac 30		Barium chlorate 25	
		Shellac 20	

The following mixture has been recommended as a flash composition, owing to its very high illuminating power, and its comparatively low sensitiveness.

Magnesium powder	..	..	..	..	50
Aluminium powder	..	..	..	..	25
Potassium perchlorate	..	..	..	..	25

STAR COMPOSITIONS FOR SIGNAL CARTRIDGES.

Illuminating.		*Red.*	
Barium nitrate 64		Strontium carbonate .. 6	
Aluminium powder .. 20		Potassium chlorate .. 16	
Sulphur 16		Calomel 2	
		Charcoal .. .. 1 to 3	
		Shellac 3	

Yellow.		*Green.*	
Potassium chlorate .. 20		Barium chlorate 24	
Sodium oxalate 6		Lactose 8	
Shellac 5		Shellac 1	

STARS USED WITH PARACHUTE STAR SHELL.

B. Composition (White).

Magnesium powder	..	..	..	..	27
Aluminium powder	..	..	..	..	9
Barium nitrate	..	..	..	..	58
Paraffin wax	..	..	..	..	6

A special composition is in use for a burning star which is visible in daylight ; and compositions also exist for similar stars giving coloured lights.

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	..	..	..	..	25
Basic copper carbonate	..	..	..	..	4
Calomel	..	..	..	..	16
Shellac	..	..	..	..	5

Rockets themselves are filled with a composition resembling gunpowder ; the composition is varied according to the speed of burning required, but a typical example is :—

Rocket Composition.

Saltpetre	..	..	..	..	85
Sulphur	..	..	..	..	1
Charcoal	..	..	..	..	14

Rockets are generally ignited by means of port fires ; these are made of a mixture of saltpetre, sulphur, and mealed gunpowder.

Flares are often provided with a special match, which is rubbed over a prepared portion of their surface in order to light them. The match head is usually a mixture of about 6 parts of potassium chlorate with 1 part of charcoal, made into a paste with shellac varnish and dried.

SMOKE COMPOSITIONS.

These 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.

Phosphorus is the usual filling for smoke shells or bombs. On bursting, the filling is ignited and scattered. The phosphorus burns to dense white fumes of phosphorus pentoxide, which hang near the ground, forming a most efficient screen of white smoke.

The following mixture is used in ground candles as a smoke producer :—

Potassium nitrate	..	..	..	..	45	
Pitch	..	..	..	..	30	
Sulphur ..	..	..	..	..	12	
Borax	..	..	..	..	9	
Glue	..	..	..	..	4	

Carbon tetrachloride, hexachlorethane, zinc dust, and zinc oxide have been suggested, and to some extent used, as active constituents in smoke producing compositions.

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 shells, sufficient smoke is evolved for purposes of observation.

Mixture, Explosive and Smoke, No. 4.			*Mixture, Explosive and Smoke, No. 7.*		
Amatol, 80/20 ..	..	1	Ammonium nitrate	..	40
Aluminium powder	..	3	Ammonium chloride	..	40
			T.N.T. ..	..	20

Tanks are able to discharge a cloud of smoke from their exhaust pipes, for screening purposes. This is accomplished by dropping chlorsulphonic acid (SO_3HCl) into the hot exhaust pipe. The acid is split up by the heat into sulphur trioxide and hydrochloric acid, both of which combine with any atmospheric moisture and cause a dense white smoke.

Coloured smoke clouds are used for day signals. They can be thrown into the air by Very pistols, or by rifle grenades. The smoke is made by the combustion of material producing a white smoke, which is coloured by the volatilisation of a suitably coloured dye-stuff incorporated in the mixture. Antimony sulphide (orpiment) is used alternatively to dye, for the production of yellow smoke.

Yellow Smoke Mixture.			*Yellow, Red, Blue or Purple, Smoke Mixture.*		
Potassium nitrate	..	33	Potassium chlorate	..	31
Orpiment	..	38	Lactose ..	..	21
Sulphur ..	..	29	Dye	..	48

These quantities are only approximate, and are somewhat varied with the different coloured dyes.

INCENDIARY COMPOSITIONS.

Illuminating compositions containing aluminium or magnesium powder, 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 howitzer bombs, or as shell fillings. In the latter case the incendiary composition, after ignition, is usually scattered by a small bursting

charge. Some incendiary mixtures, such as thermit, are hard to ignite, and must be initiated by a suitable priming material.

The requisite essential of an incendiary mixture is, a very high temperature of combustion, or a persistent flame effect. When ignited, such a mixture should be difficult to extinguish.

Shells and bombs may be filled with carcass composition. This is effective against readily inflammable material; it does not give a very high temperature, but relies on the long flames produced. The proportions of the ingredients have been altered from time to time, and the proportions given are thus only approximate.

Carcass Composition.

Saltpetre	50
Sulphur	20
Resin	15
Antimony sulphide :.	5
Russian tallow	5
Venice turpentine .. .. .. ,.	5
Mealed black powder	8
Aluminium powder	40

Incendiary shells may be filled with magnesium mixtures; by the addition of certain metallic salts, these may be made to give a distinguishing coloured light during combustion.

COMPOSITIONS FOR INCENDIARY SHELLS.

S.R. Composition 512.   *S.R. Composition, 260.*

Yellow during burning.   *Red during burning.*

Magnesium powder ..	28	Magnesium powder ..	35
Paraffin wax	6	Paraffin wax	6
Sodium nitrate	50	Strontium nitrate ..	48
Powdered ivory nut ..	16	Wood meal	11

For use against less readily inflammable material, thermit is used as an incendiary.

Military Thermit.

Magnetic iron oxide (Fe_3O_4)	76
Aluminium powder (or flake)	24

When ignited the two substances interact; no gas and practically no flame is evolved, but there is a great evolution of heat, which is retained in the mixture of molten iron and aluminium oxide. This may be scattered by a small bursting charge, and then has great incendiary effect. If not scattered, the effect is local, owing to the absence of flame; but in this case thin sheets of metal may be perforated by the extreme temperature of the molten material.

H.—SAFETY PRECAUTIONS.

Chapter XVIII.

SAFETY PRECAUTIONS.

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 emphasising 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.

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 unauthorised 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.

Regulations have been drawn up by H.M. Inspectors of Explosives laying down the minimum distance permissible between adjacent buildings. 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. For instance, in Austria, for the purpose of these regulations, buildings are relegated to one of two classes :—

> (1) Buildings which are remote from other centres of activity, and which do not contain fires ; and

> (2) Buildings which are near populated centres, or near railways, roads and paths where an explosion might have disastrous consequences.

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.

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.

For artificial lighting, electric lamps are almost always employed. They should be 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 so arranged that any accident which shatters the globe of the lamp also fractures the filament and so cuts off the current.

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.

2. Each piece of metal in the building should be " earthed " and insulated from the main structure. Sharp points on different masses of metal across which a spark may jump should be avoided, or separated by as great a distance as possible. This danger may be minimised by electrically connecting all the masses of metal in the building.

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 to electrically " 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, &c., at the entrance. This provision is enforced by giving some principal official the right to search or to authorise 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 become frozen and may 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. If the buildings are solidly constructed, and well covered with earth, the temperature does not vary sensibly throughout the 24 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	..	..	..	·3	1·3

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, &c., 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 more dangerous from the risk it entails of a gas explosion than for any other reason. This gas explosion may be sufficiently violent to break down partitions, and so cause the ignition of explosives stored in adjacent compartments. Therefore, either (1) the walls, floors and roof must be made strong enough to withstand the pressure of a gas explosion, or (2) explosives liable to ignition by a gas explosion must not be stored in the vicinity.

The action of stabilisers 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, 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. Water alone may not suffice for cleansing, and the use of various reagents such as acetone and caustic soda, according to the explosive likely to be present, may be necessary.

APPENDICES.

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APPENDIX 1.

(1) Thompson. "*Guide to the Explosives Act*, 1875."

(2) G. S. Rice. U.S.A. Bureau of Mines, 1920 :—
"*Development of Liquid Oxygen Explosives during the War*."
"*Revue de Chimie indust.*, 1919," Vol. 28, p. 408.

(3) R. H. S. Kempton. "*Nitrogen and its Industrial Applications*."
"*Report of the Nitrogen Committee*, 1920," and Supplement, 1921.

(4) R. C. Farmer. "*The Manufacture and Uses of Explosives*." 1921.

(5) Lieut.-Col. Crozier in *R.A. Journal*, Vol. XLVI, No. 9.

(6) Noble. *Proceedings of the Royal Society*, 1905, p. 381.

(7) R. C. Farmer. "*The Manufacture and Uses of Explosives*." 1921. P. 26.

(8) T. Martin Lowry. "*Inorganic Chemistry*." Macmillan, 1922.

(9) "*Army Ordnance*" (Journal of the Army Ordnance Association, U.S.A.),
Vol. III, p. 273.

(10) "*Text-Book of Anti-Aircraft Gunnery*." Vol. I.

(11) A. Marshall. "*Dictionary of Explosives*." J. & A. Churchill, 1920.

APPENDIX II.

TABLE II.A.—TABLE OF PHYSICAL CONSTANTS FOR EXPLOSIVES.

Note.—The gram-calorie is used in this table.   P/A = Picric Acid.

Explosive.	Specific Gravity at 15·5° C.	Figure of Insensitiveness. P/A = 100.	Rate of Detonation in Metres/Second (at Density).	Melting Point.	Ignition Point.	Volume of Total Gases (c.c./gram).	Heat of Decomposition (Gram-calories per Gram/Water Gaseous).
Amatol 40/60	1·70*	115	6,470 (Cast 1·55)	76° C.	242° C.	892	920
Amatol 80/20	1·71*	120	4,620 (1·3) 5,080 (1·5)	Softens at 76° C.	235° C.	907	1,004
Ballistite	—	14–16 (?)	Up to 5,200 with greater confinement	—	166° C.	800	1,136
Cordite Mark I	1·57	94	—	—	151° C.	886	1,114
Cordite M.D. and M.C.	1·58	56	—	—	160° C.	933	939
Cordite R.D.B.	1·54	61	—	—	155° C.	959	904
Dinitrophenol	1·67	Over 120	6,100	110° C.	Over 250° C.	—	—
Guncotton, Dry	1·67	23	7,300 (1·2)	—	187° C.	830	960
Guncotton, Wet (13 per cent. water)	1·54	120	About 5,500 (1·1)	—	—	859	770
Gunpowder	—	65	—	—	About 300° C.	256	726

TABLE II.A.—TABLE OF PHYSICAL CONSTANTS FOR EXPLOSIVES—*continued.*

Explosive.	Specific Gravity at 15·5° C.	Figure of Insensitiveness P/A = 100.	Rate of Detonation in Metres/Second (at Density).	Melting Point.	Ignition Point.	Volume of Total Gases (c.c./gram).	Heat of Decomposition (Gram-calories per Gram/Water Gaseous).
Lyddite (fused trinitrophenol) ...	1·77	100	7,250 (1·63)	120° C.	Over 250° C.	744	914
Lead azide	4·8	20	3,500 (?)	—	320°–390° C.	230	~~370~~ 363
Mercury fulminate	4·43	10	3,000 (loose)	—	147° C.	240†	~~410†~~ 404
Nitroglycerine	1·6	13	7,500 to 8,000	13° C. Rhombic form	170°–180° C.	713	1.478
Nitrocellulose powder (·5 per cent. diphenylamine)	1·6	—	—	—	152° C.	961	777
Picric powder	—	87	—	—	—	—	—
Tetryl (C.E.)	1·77	70	7,520 (1·63)	129° C.	180° C.	794	1,090
Trotyl (T.N.T.)	1·68	115	6,950 (1·57)	76°–80° C.	240° C.	728	924

* Calculated.   † Mercury liquid.   (?) Not reliable.

TABLE II.B.—RESULTS OF MEASUREMENTS MADE BY THE PRESSURE BAR TEST.

Explosives.					Weight.	Density.	Container.	Shaft Protection.	Pressure.
									Tons/sq. in.
T.N.T., Grade I	...	...	...	...	47·3 grams	1·3	Bomb, ¼-in. wall, with cap	Asbestos pellet, Length 1·55 ins. Δ = 1·3	42·3
T.N.T., Grade I	...	...	...	...	41·7 grams	1·2	Paper.	Do.	13·2
C.E., Grade I	...	...	...	...	47·3 grams	1·3	Bomb, ¼-in. wall, with cap	Do.	46·2
C.E., Grade I	...	...	...	...	41·7 grams	1·2	Paper	Do.	14·2
Amatol 40/60	...	...	...	...	48·1 grams	Cast	Bombs, ¼-in. wall, with cap	Do.	41·9
Amatol 80/20	...	...	...	...	47·3 grams	1·3	Bombs, ¼-in. wall, with cap	Do.	36·9
Amatol 80/20	...	...	...	...	41·7 grams	1·2	Paper	Do.	10·8
Mercuric fulminate		...	...	...	4 grain	—	4-grain shell, in brass holder	0·20 ins.	9·56
Mercuric fulminate		...	...	...	5 grain	—	5-grain shell in brass holder	0·20 ins.	12·6
Lead azide, with 6.6.4 composition			...	...	3½ grains lead azide	Pressed 1,000 lbs per sq. in.	5-grain shell in brass holder	0·20 ins.	9·26
					1½ grains 6.6.4	Pressed 900 lbs. per sq. in.			
Lyddite	...	...	...	...	47·3 grams	1·3	Bomb, ¼-in. wall, with cap	Asbestos pellet, length 1·55 ins. Δ = 1·3	45·3
Lyddite	...	...	...	...	41·7 grams	1·2	Paper	Do.	11·85
Gunpowder	...	...	...	...	51 grams	1·45	Bomb, ¼-in. wall, with cap	Do.	8·2

APPENDIX III.

GLOSSARY OF TERMS.

Analysis.—The determination of the composition of a substance, by its conversion into other compounds which can be recognised. *Qualitative analysis* determines the *nature* of the constituents ; *quantitative analysis* the *proportions* in which they are present.

Absolute Temperature.—*See* **Temperature, Absolute.**

Autoclave.—A vessel in which chemical actions can be performed at high pressures, the pressure being produced by the evaporation of liquid in the vessel.

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.

Catalyst. Catalytic Action.—A substance which accelerates a chemical action, but which is itself unchanged at the end of the process. *Catalytic action* : the operation of a *catalyst*.

Centrifuge.—A machine used for separating substances (1) of different densities and (2) of different states by the action of centrifugal force. The substances are contained in a cylindrical vessel which can be rotated at a high speed. The denser material is driven to the outside, whence it may be withdrawn. Familiar examples of a *centrifuge* are to be found in (i) the cream separator, and (ii) the centrifugal drier used in laundries.

Counter-current Methods.—Methods by which two liquids 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 process of nitrating M.N.T. to T.N.T. described on pages 56 and 57 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 : $\dfrac{\text{Weight of charge in the chamber (in grams).}}{\text{Weight of water which would fill the chamber (in grams).}}$

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 proximate may be separated at one operation.

Distillation, Steam.—Substances which would char if heated strongly but which vaporise 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 vaporised 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 will be found on page 12.

Endothermic Compound.—A compound which absorbs heat on its formation. An example will be found on page 13.

Exothermic Action.—A chemical action in which heat is liberated. An example will be found on page 13.

Exothermic Compound.—A compound which liberates heat on formation. An example will be found on page 14.

Ester.—An organic salt formed by the interaction of an acid and an organic compound containing a replaceable hydroxyl (-OH) group or groups. The acid may be organic or inorganic. Compare the formation of inorganic salts.

Examples :—

(i) Inorganic Salt.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
$$\text{Salt.}$$

(ii) Esters.

a. $C_2H_5 . OH + HCl \longrightarrow C_2H_5 . Cl + H_2O$.
$$\text{Ester.}$$

b. $C_2H_5 . OH + CH_3 . COOH \longrightarrow CH_3 . COO . C_2H_5 + H_2O$
$$\text{Ester.}$$

c. $\begin{array}{l} CH_2OH + HNO_3 \\ | \\ CH . OH + HNO_3 \\ | \\ CH_2OH + HNO_3 \end{array} \longrightarrow \begin{array}{l} CH_2NO_3 \\ | \\ CH . NO_3 \\ | \\ CH_2NO_3 \end{array} + 3H_2O$.
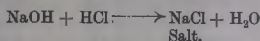
Ester.
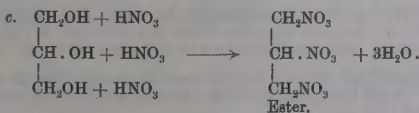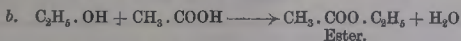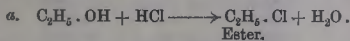
a. represents the action of hydrochloric acid on ethyl alcohol to form ethyl chloride and water.

b. represents the action of acetic acid on ethyl alcohol to form ethyl acetate and water.

c. represents the action of nitric acid on glycerine to form glyceryl trinitrate (nitroglycerine) and water.

Eutectic.—A mixture of two substances which has the lowest melting point of any possible mixture of the two constituents and in which the two components are structurally distinct.

Fractional Distillation.—*See* **Distillation, Fractional.**

Gram-Molecule.—The molecular weight, in grams, of a substance.

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. If the substance is a salt or an ester the process is the reverse of **Neutralisation.** For example :—

$$Zn(OH)_2 + H_2SO_4 \qquad ZnSO_4 + H_2O .$$
$$\text{Neutralisation.} \longrightarrow \qquad \longleftarrow \text{Hydrolysis.}$$
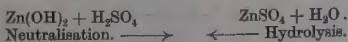
Hygroscopic.—A substance capable of absorbing moisture from the air and retaining it is said to be Hygroscopic, *e.g.*, ammonium nitrate. $(NH_4NO_3.)$

I.M.M. Sieves.—These sieves are standardised by the Institute of Mining and Metallurgy. A table of wire diameters and aperture sizes is given below for reference.

Table of I.M.M. Standard Laboratory Screens.

Mesh apertures per linear inch.	Diameter of Wire.		Aperture.	
	inch.	m.m.	inch.	m.m.
5	0·1	2·540	0·1	2·540
8	0·063	1·600	0·062	1·574
10	0·05	1·270	0·05	1·270
12	0·0417	1·059	0·0416	1·056
16	0·0313	0·795	0·0312	0·792
20	0·025	0·635	0·025	0·635
30	0·0617	0·424	0·0166	0·421
40	0·0125	0·317	0·0125	0·317
50	0·01	0·254	0·01	0·254
60	0·0082	0·211	0·0083	0·211
70	0·0071	0·180	0·0071	0·180
80	0·0063	0·160	0·0062	0·157
90	0·0055	0·139	0·0055	0·139
100	0·005	0·127	0·005	0·127
120	0·0041	0·104	0·0042	0·107
150	0·0033	0·084	0·0033	0·084
200	0·0025	0·063	0·0025	0·063

Isomeric.—Having the same composition by weight, 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**.

Kilowatt-year.—An electrical unit of work or energy. The Board of Trade " unit " is the *kilowatt-hour*. Thus 1 *kilowatt-year* = 8,760 *kilowatt-hours* = 11,738·4 *horse-power hours*.

Molecular Heat of Formation or Decomposition.—The amount of heat, measured in Calories, given out or absorbed in the formation or decomposition from or into its constituent elements of 1 gram-molecule of a substance.

Molecular Heat of Explosion or Combustion.—The amount of heat, measured in Calories given out or absorbed on the explosion or combustion of 1 gram-molecule of a substance. If water is one of the products of explosion or combustion, it must be stated whether the water is considered as a gas (steam at 100° C.), or as a liquid.

Mother Liquor.—The impure liquid remaining after a substance has crystallised 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.N.O$_2$). 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 :—

$$H_2 C—O—N—O_2.$$
$$H—C—O—N—O_2.$$
$$H_2 C—O—N—O_2.$$
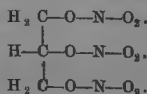
Nitro-compound, nitro-body.—Compounds in which the nitro group (-NO₂) is introduced by replacement, usually of hydrogen. In organic *nitro-compounds*, the nitrogen is linked directly to carbon, *e.g.*, tri-nitro-toluene :—

$$
\begin{array}{c}
CH_3 \\
| \\
C \\
O_2N-C \quad\quad C-NO_2 \\
\| \quad\quad\quad | \\
H-C \quad\quad C-H \\
C \\
| \\
NO_2
\end{array}
$$
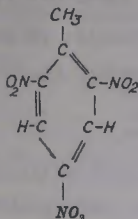
Reversible Reaction.—A reaction which may proceed in either of two directions according to the conditions under which it is performed, *e.g.*,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 . \quad (\textit{See} \text{ page 60.})$$
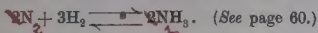
Specific Heat.—The amount of heat required to raise unit mass of a substance through unit interval of temperature. If measured in Calories, it is the amount of heat required to raise 1 kilogram of a substance through 1° C. With gases there are two principal *specific heats* according as the determination is made at constant pressure (C_p) or at constant volume (C_v).

Steam Distillation.—*See* **Distillation, Steam.**

Synthesis.—The formation of a substance by artificial methods as distinct from its production from natural sources *e.g.* " *synthesis* " of ammonia. (*See* page 60.)

Temperature, Absolute.—The *absolute zero* is the temperature at which a perfect gas would occupy zero volume. On the Centigrade scale this is −273° (−459° F.).

Unsaturated Compounds.—Compounds which are capable of combining with other compounds or elements by addition, there being no formation of substitution products, *e.g.*,

$$
\begin{array}{cc}
C_2H_4 + Cl_2 \longrightarrow & C_2H_4Cl_2 . \\
\text{Ethylene.} & \text{Ethylene Dichloride.}
\end{array}
$$
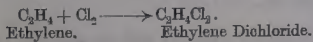
Water Equivalent of a Body.—The weight of water which can be raised through a given interval of temperature by the amount of heat required to raise the body through the same interval of temperature. It is the product of the mass of the body and its specific heat.

APPENDIX IV.

A SHORT DICTIONARY OF EXPLOSIVES (11).

Ammonite.—A coal-mine explosive. A modern variety of this explosive has the following composition :—

Ammonium nitrate...	...	...	...	...	74·5
Trinitro-naphthalene	...	...	...	...	5
Sodium chloride	...	...	...	...	20·5

The use of *trinitro-naphthalene* should be noted.

Bellite.—A coal-mine explosive employing *meta-dinitro-benzene*.

Ammonium nitrate...	...	...	...	...	63·5
Dinitro-benzene	...	...	...	...	15
Sodium chloride	...	...	...	...	16·5
Starch	...	...	...	...	5

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

Bobbinite.—A very widely used coal-mine explosive of the nature of gunpowder. It is not suitable for use in gassy mines.

Potassium nitrate	...	...	...	...	65
Charcoal	...	...	...	...	20
Sulphur	...	...	...	...	2
Rice or maize starch	...	...	...	...	9
Paraffin wax	...	...	...	...	3
Moisture	...	...	...	...	1

Another variety differs from the above, in the replacement of the *starch* and *wax* by *ammonium and copper sulphates.*

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 extremely insensitive to blows and friction, 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.

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.

Ecrasite.—An Austrian military high explosive consisting of the *ammonium salt* of *trinitro-cresol*.

Faversham Powder.—Originally consisted of 90 per cent. *ammonium nitrate* and 10 per cent. *T.N.T.* It therefore was an amatol. Later variants contained *potassium nitrate* and *ammonium chloride* in addition to the above.

Fulminate of Silver.—AgONC. The silver salt of fulminic acid. It is made in a similar manner to mercuric fulminate. It is, however, very much more sensitive. Its use is confined to toy fireworks, crackers, &c., which are not allowed to contain more than a very limited amount.

Fulminating Mercury.—Hg_3N_2.

Fulminating Silver.—Ag N. ⎱ Are the nitrides of mercury and silver.

They are made by treating the respective oxides with ammonia. They are too sensitive for general use as explosives.

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 stabiliser.

Gelignite is very similar to gelatine dynamite, but contains a reduced proportion (60%) 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 sometimes introduced. These substances have the effect of depressing the freezing point of the nitroglycerine.

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 oxidising agents, it forms a powerful high explosive. It is, however, too unstable for general use.

Judson Powder.—A blasting powder, not used in this country, consisting of low grade gunpowder coated with nitroglycerine. The percentage of nitro-glycerine varies from 5 to 20.
The following is an analysis of one variety :—

Nitroglycerine ...	...	...	...	...	...	5
Sodium nitrate...	...	...	...	...	...	64
Sulphur...	...	...	...	...	...	16
Cannel coal	...	...	...	...	...	15

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 fillings 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 *nitro-toluene* are the constituents. It is very powerful and violent but dangerous to handle owing to the poisonous 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

Pierrite.—A form of cheddite which is noteworthy for its employment of *picric acid*.

Potassium chlorate	80
Nitro-naphthalene	11·5
Picric acid	2
Castor oil	6·5

Poudre B.—The French Service propellant. It consists of *nitrocellulose* gelatinised with ether/alcohol. Diphenylamine is used as a stabiliser. 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* gelatinised 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 latter 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
            Naptha   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~~ 87·4 .
      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 *oxidising agent* and a *combustible*, which are segregated until required for use. In this way, all danger of premature explosion is eliminated.

Suitable oxidising 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.**

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USED IN THE SERVICE.

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