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CHEMICAL DISCOVERY  
AND INVENTION

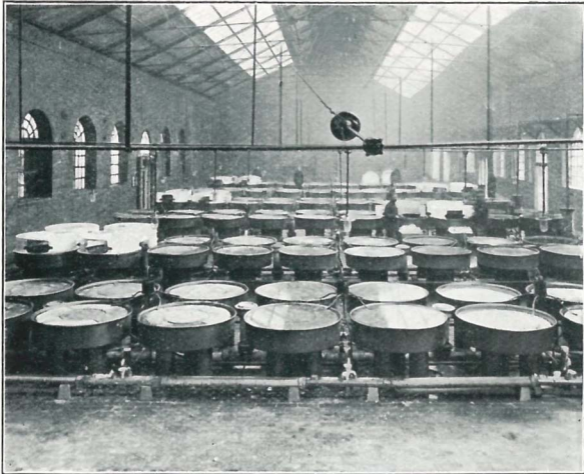


FIG. 138.—DISPLACEMENT PROCESS. WALTHAM ABBEY

WAC 1828

# CHEMICAL DISCOVERY AND INVENTION

IN THE TWENTIETH CENTURY

By

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nozzles in the form of rods, tubes, and strips. If sheets are required the strips are either flattened out by pressure whilst heated, or else they are forced together by heat and pressure into a block from which thin slices may be cut by means of a special planing machine. The casein material is now immersed in a 5 per cent formalin bath for some time to harden; it is finally removed and dried in hot air. In this final form the plastic can either be turned or drilled on a lathe, or it can be softened in hot water and so moulded or stamped. The casein plastics can be produced in a remarkably beautiful range of colours, and the material takes a high polish; it is used specially for buttons, but there are many other applications, such as for fountain pens, pencils, small electrical parts, knife handles, and imitation tortoise shell. As it softens in hot water the casein plastics cannot be used for domestic utensils.

The "solvent naphtha" fraction obtained from coal-tar distillation contains a number of substances for which little use was found until recently. Amongst these may be mentioned particularly the related compounds *coumarone* and *indene*, which distil over between 168° and 182° C.; it has been known for over forty years that if to these substances is added a small quantity of concentrated acid a polymerisation process occurs, that is to say several simple molecules unite to form a large, complex molecule, and the product is a resinous substance now known as "coumarone resin" or "cumar." This material dissolves in hot linseed oil as well as in spirit, and on drying leaves a very hard film; it is consequently replacing copal gum and shellac in the paint industry. In the United States cumar resin is also used in the manufacture of "chewing gum."

In addition to the synthetic plastics and resins already mentioned others of minor importance, at the moment, are being made commercially or are being tried out experimentally. Of these mention may be made of benzyl cellulose, still another derivative of cellulose to find industrial application. Before closing this chapter, however, it will be of interest to give some idea of the extent of the artificial plastics industry; apart from the production of celluloid which does not really belong to the present century. In 1923 there were produced in Great Britain about a million pounds weight of phenol-formaldehyde resins, but in 1933 the amount had increased tenfold; in the United States the corresponding figures are 11,000,000 lbs. in 1923, and

31,000,000 lbs. in 1933, the latter amount being below the record production of 34,000,000 lbs. in 1931. Although the bakelite type of resin represents the greatest proportion the others are also made in considerable quantities, and some figures of production have been already given. It will be seen that in the manufacture of artificial plastics a vast industry has arisen from a few apparently unimportant and trivial observations made generally before the present century. For the reader who wishes further information on the subject of plastics the special journals, such as *British Plastics*, as well as text-books on the subject, should be consulted.

## CHAPTER XXVI

## EXPLOSIVES

“ . . . it was great pity, so it was,  
This villainous saltpetre should be digg'd  
Out of the bowels of the harmless earth,  
Which many a good tall fellow had destroy'd  
So cowardly; and, but for these vile guns  
He would himself have been a soldier.”

WHEN Shakespeare put these words into the mouth of Hotspur the only use for gunpowder was in the practice of war, and for purposes of destruction such as was contemplated in the Gunpowder Plot of 1605. But though the mention of explosives immediately suggests war, it must not be forgotten that these agents have been among the most powerful auxiliaries in the arts of peace. It is only necessary to consider how many roads, railways, tunnels, and water works have been rendered possible by the use of dynamite and other blasting materials to perceive that explosives have a civilising mission of their own, and probably next to steam have done more to facilitate inter-communication between different countries than any other of the works of man's invention. The importance of explosives to industry will be realised when it is remembered that nearly half a million tons are used in the world each year in times of peace.

The chemist of the twentieth century is acquainted with a large number of substances which when heated or struck or in some cases even merely shaken explode, but the great majority of them are useless for practical purposes, being too unstable to

be handled or carried about without great danger to the person. By an explosion the chemist understands the sudden production of a relatively large volume of a gas or gases from a solid, liquid, or mixture of gases. And as such changes are almost always attended by the production of much heat, the hot gases formed are still further expanded. For the moment the last case must be postponed from consideration, but the reader will easily understand what is referred to by thinking of the disastrous effect in a coal-pit when a mixture of air with inflammable gas from the coal, called *fire-damp*, comes into contact with a flame. The resulting explosion which, under such circumstances, does nothing but mischief, can in another form be turned to useful practical account when under control in the gas-engine or internal combustion engine of the motor.

But although explosive substances are familiar in the chemical laboratory, and have multiplied among the products of modern chemical research, it is curious to note that nearly all the explosives employed as propellants or for blasting purposes are produced more or less directly by the use of the "villainous saltpetre" so long an ingredient in old-fashioned black gunpowder. The object in all cases is to introduce into a mixture or compound containing the combustible elements, carbon and hydrogen, so large a quantity of oxygen that the product will burn without the assistance of atmospheric air.

This is effected in the case of gunpowder through the agency of the nitre or saltpetre which supplies oxygen to the sulphur and charcoal with which it is mixed. Or it may be by bringing cotton or glycerine or phenol or some other compound of this kind into contact with nitric acid. An interchange is then effected whereby a portion of the hydrogen of the original substance is removed in the form of water and a group of atoms characteristic of the nitrates is introduced. When the nitrated compound is fired the oxygen combines with carbon forming gaseous oxides of carbon, and with the hydrogen forming water, which is of course liberated in the form of steam, while the nitrogen is set free in the state of gas and thus contributes to the total volume of gas formed in the act of explosion.

This chapter must be devoted to an account of the chemical composition and action of the modern explosives, some of them of quite recent introduction, but to understand why some of the changes which have taken place of late years have been intro-

duced, it is necessary in passing to glance at the changes which have taken place in the construction of military and naval guns.

At the time of the Crimean War the largest guns ashore or afloat were the 68-pounders with smooth bores. The idea of rifling the gun for the purpose of giving the projectile the spin which increases greatly its accuracy of fire had not at this time been actually adopted in practice. With this very important change two names will always be connected, the late Lord Armstrong (died 1900) and the late Sir Andrew Noble (died 1915), who for some forty years were associated together in the great Elswick Ordnance Works near Newcastle-on-Tyne. To the former we owe the rifled breech-loading gun with wire-wound cylinder, to the latter the invention of the chronoscope, by which minute fractions of time may be measured, beside famous experiments on the pressures attained in large guns.

Up to about 1886 black gunpowder had been used, but as it had been found that with increased length of the gun the pressure on the breech became injurious to the gun without giving the desired velocity to the projectile, many modifications were tried in the size of the grain, and in the cubes, prisms or perforated slabs in which form the powder was used. The old powder, however, had one inseparable defect, namely, the large quantity of smoke produced in firing. This arises from the fact that black gunpowder is composed of nitre, charcoal, and sulphur in the proportions on the average of 75 : 15 : 10 per cent respectively. Hence when burnt the potassium of the nitre is converted into a mixture of potassium carbonate, potassium sulphate, with a small quantity of potassium sulphide, all of which are solids, and being dispersed in fine powder give rise to clouds of smoke. At the time referred to the service powders used by the various European Powers had the composition shown in the following table :

Country.	Nitre.	Charcoal.	Sulphur.
England Black Powder . . . . .	75	15	10
„ „ Brown „ . . . . .	79	18	3
Sweden . . . . .	75	15	10
Russia . . . . .	75	15	10
Prussia . . . . .	74	16	10
Saxony . . . . .	74	16	10
United States . . . . .	76	14	10
Austria . . . . .	75.5	14.5	10
France . . . . .	75	12.5	12.5

According to Thorpe's *Dictionary of Applied Chemistry* Chinese gunpowder contained nitre 61.5, charcoal 23, and sulphur 15.5 parts per cent. This departure from the type, which has been established by modern scientific methods of manufacture, is interesting when the tradition is recalled which attributed the invention of gunpowder to the Chinese.<sup>1</sup>

Changes in the guns then demanded changes in the rate of combustion of the powder used in them, while the conditions of modern warfare required a propellant which should be practically smokeless. It seemed useless to construct quick-firing guns and machine guns capable of delivering a shower of bullets if after the first discharge or two all view of the enemy in front of the guns became impossible. Gun-cotton, which is the essential basis of all modern propellants, differs from the old powder in yielding only gaseous products in its explosion, without any solid and hence without smoke. There is also an important difference between the two, in the fact that the old powder is merely a mechanical mixture of solid ingredients, the particles of which, under a microscope, can be seen lying side by side but quite distinct from one another, while gun-cotton is a chemical compound. In the former, therefore, the oxygen required to combine with the sulphur and with the carbon of the charcoal has to be liberated first from the particles of the nitrate and then to attack separately the particles of the combustible sulphur and carbon.

In gun-cotton and similar substances, each molecule of the compound contains within itself the elements which are to combine together to form the gaseous products of the explosion.

This will be understood by reference to the equation given below.

As already stated in an earlier chapter, clean cotton consists of almost pure cellulose, which has the formula  $(C_6H_{10}O_5)_n$ ,

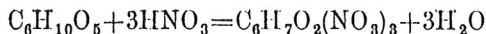
<sup>1</sup> The invention of gunpowder is by the English attributed to Roger Bacon, who was born in 1214. Others suppose a certain monk, of whom nothing positive is known, but who is supposed to have lived in the early part of the fourteenth century, to have been the inventor. He is commonly spoken of as Berthold Schwarz, a purely imaginary name.

Gunpowder and cannon were known to have been used in England in 1344, in France in 1338, and the Oxford MS. "De officiis regum," dated 1325, gives an illustration of a gun. The invention of gunpowder must therefore be placed at an earlier date.

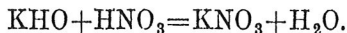
Those who are interested in the history of the subject should consult *Monumenta Pulveris Pyrii*, by the late Oscar Guttmann, 1906.



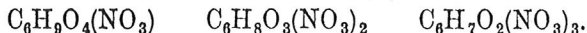
where  $n$  is a large number ; there is in addition a small amount of mineral matter, as may be seen from the ash left when the cotton is burnt away. When cotton is immersed in strong nitric acid an interchange takes place which may be expressed by the following equation :



in which it is obvious that the product is a nitrate, and its formation is comparable with the production of a nitrate when caustic potash is mixed with nitric acid. Water is in both cases formed simultaneously :



In the case of cellulose three stages of nitration are possible, the products being represented by formulæ, thus :



Gun-cotton or nitrocellulose, which should more strictly be called cellulose nitrate, consists mainly of the last of these three substances, the trinitrate.

It has long been known that when starch, paper, cotton fibre, or other vegetable material is soaked in very strong nitric acid and is subsequently washed in water and dried, the cotton or other material is scarcely changed in appearance, but it is found to have increased in weight, 1 part of cotton giving, according to the theory explained above, 1.8 parts of nitrated cotton. This material is extremely inflammable, and on contact with a flame disappears instantaneously with a bright flash. The Swiss chemist Schönbein, so long ago as 1845, proposed to use this product as a substitute for gunpowder. It was, however, many years before the manufacture of gun-cotton could be carried on without danger of explosion, and before the product could be obtained in a condition in which it could be stored and used for any purpose with reasonable safety. A long series of experiments, conducted first by the Austrian General von Lenk, and later by Sir Frederick Abel in this country, led to the discovery of the conditions necessary for this object, the first essential being the removal of the last traces of acid from the nitrated cotton.

At the present day gun-cotton as well as nitroglycerine, to be described later, is manufactured in large quantities in many

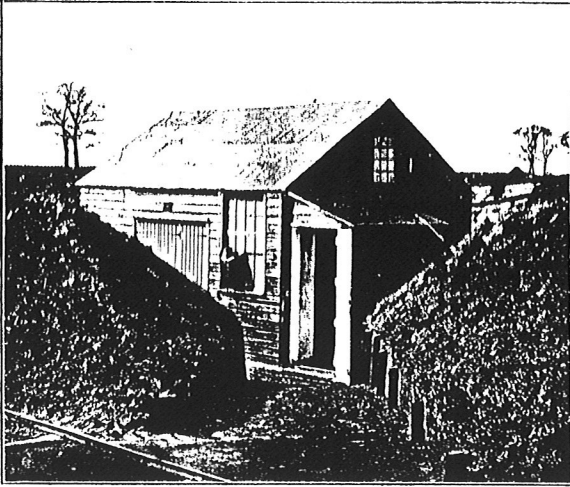


FIG. 116.-- MOUNDED HOUSE, COTTON POWDER WORKS

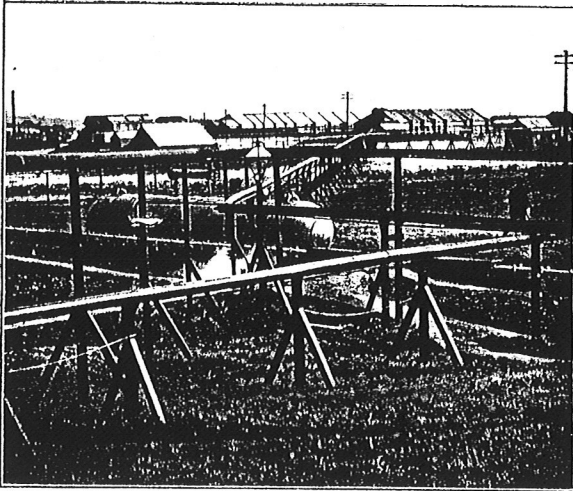


FIG. 117. BUILDINGS AND PIPE CONNECTIONS  
COTTON POWDER WORKS

countries in which the regulations controlling the operations vary. In the United Kingdom the Explosives Department of the Home Office prescribes the conditions which must be obeyed.

In laying out explosives works it is necessary to distinguish the danger area from the non-danger area. In the latter, boilers, engines, acid stores, and other departments may be arranged in any manner found to be most convenient, but in the former where the manufacture of the explosive is carried out the case is quite different. Restrictions are imposed in order to prevent the introduction of any materials likely to set off the explosive material. The buildings are so arranged as to allow only limited quantities of explosive material and a limited number of work-people in one building at a time, and further to place the different buildings at such distances from each other, or surround them by protecting earth mounds (Fig. 116), that in the event of an explosion the amount of damage and loss of life is reduced to a minimum.

The manufacture of gun-cotton and the other forms of nitro-cellulose is carried out in the first stages in the non-danger part of the factory. The raw material is cotton waste, which is specially prepared for the explosive manufacturer. First it is hand picked in order to remove all foreign matter as much as possible, and it is amazing to see how much rubbish in the form of pieces of wire, wood, nails, etc., is thus removed. Next it is teased and dried, because cotton ordinarily contains about 10 per cent of moisture and this water would needlessly dilute the nitrating acids. The photograph (Fig. 118) shows a drying-plant in use at Waltham Abbey. Here it is exposed to a temperature of about 80° C. for twenty minutes. It is then weighed up, according to the older method introduced by Sir Frederick Abel, into lots of 1½ lb. called a charge, and is kept dry in an air-tight box till it is dipped.

The acids used consist of a mixture of 1 part by weight of strong nitric acid of specific gravity 1.5, with 3 parts by weight of strong sulphuric acid of specific gravity 1.84. Mixing the acids is attended by evolution of heat and the mixture is allowed to become completely cool before it is run into the cast-iron dipping tank.

The charges of cotton are immersed in the acid for a few minutes, then placed on a grating and the excess of acid squeezed out. The partially changed cotton, still saturated with acid, is

*Investigated  
by 1756*

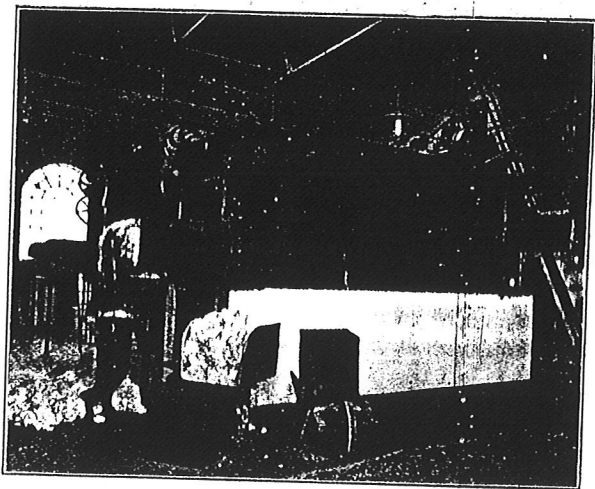


FIG. 118.—DRYING MACHINE, WALTHAM ABBEY .

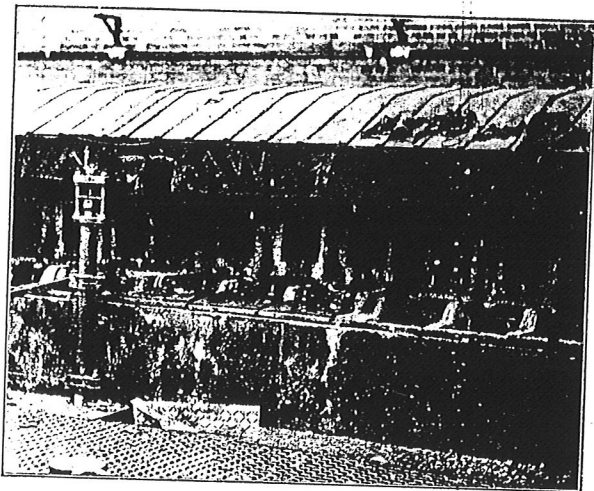


FIG. 119.—ABEL NITRATION PROCESS. DIPPING PANS  
WALTHAM ABBEY

placed in an earthenware covered pot standing in water, and left for about twelve hours (Fig. 119). The nitration is then complete, and the contents of the pots are lifted out by tongs and placed in a centrifugal machine, where the excess of acid is wrung out. The gun-cotton is then placed in a tank full of running water till the water no longer answers to a test for acid.

To remove the last traces of acid the cotton requires to be boiled with water repeatedly. It is then reduced to pulp which, suspended in water, is passed by a pipe into the "poaching" machine, where paddles keep the fine pulp agitated with water and thoroughly wash every portion of it. After some hours a small quantity of lime-water, whiting, and caustic soda is added so as to leave the cotton pulp slightly alkaline. It is then drawn off by means of a vacuum pump, and the pulp strained off in measured quantities into moulds, where pressure is applied sufficient to reduce the substance to the condition of a solid cake hard enough to bear handling. Finally, the moulded cotton is submitted to hydraulic pressure amounting to about five tons on the square inch, which leaves the cake so hard that it does not yield perceptibly to pressure by the finger.

Newer methods of nitration have been introduced by which a larger quantity of cotton can be immersed in the acids at one time.

Centrifugal machines have been constructed which can be filled with the acids and a much larger weight of cotton, generally about 17 lbs., can be immersed. When the nitration is complete the acid can be run off and the cotton drained by setting the machine in motion.

Another method employed at the Royal Factory, Waltham Abbey, is known as the displacement process. The plant consists of shallow earthenware circular pans grouped together in sets of four. They are provided with perforated false bottoms, and the bottom of each pan is connected with a pipe by which the nitrating acid can be supplied, and a pipe by which the spent acid can be drawn off. These pans will each take a charge of 20 lbs. of dry cotton.

When all the cotton is immersed perforated earthenware plates are laid on top of the cotton to keep it under the acid, and a thin layer of water is cautiously run over the surface which prevents the escape of acid fumes. After two and a half hours the nitration is complete; the spent acid can be drawn off, and an

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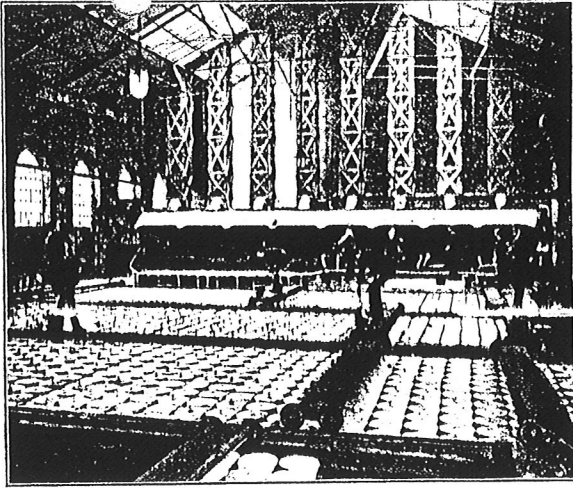


FIG. 120. ABEL NITRATION PROCESS, WALTHAM ABBEY

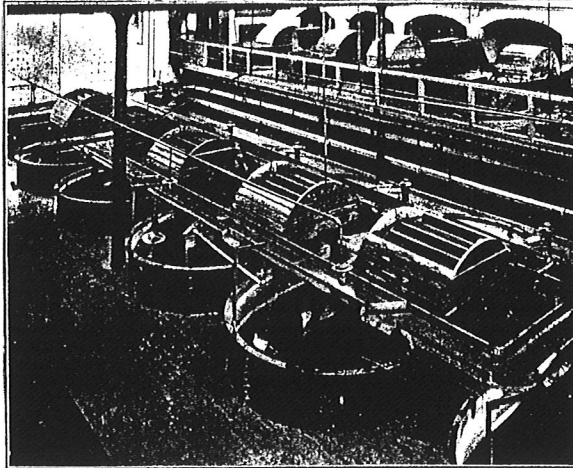


FIG. 121.—BEATING ENGINES AND POACHER  
WALTHAM ABBEY

equivalent quantity of water run into each pan. In this way the spent acid is displaced much more completely than by the older methods.

After draining off the water from the pans the gun-cotton is ready for the processes of purification already described.

In some factories a continuous process for nitrating cellulose is used; the latter is formed into a continuous band and passed at the appropriate speed through the bath of nitrating acid, so as to give the desired extent of nitration. Fresh acid is added to the bath continuously in order to maintain its concentration. The nitrated cellulose is then washed carefully to remove excess of acid.

Up to this point the nitrated cotton has been treated as non-explosive, but in order to dry it, it is removed to one of the stoves in the danger area. Dry gun-cotton is one of the most dangerous explosives, as when dry and warm it is very liable to explode by friction, and the greatest care has to be exercised in handling it.

In the production of gun-cotton the composition of the acid mixture is of the utmost importance, and if the sulphuric acid present is deficient in amount, or the proportion of water formed in the process is allowed to exceed a certain amount the nitration does not reach the maximum. Nitrocellulose having the composition expressed by the formula given above contains just over 14 per cent of nitrogen. Gun-cotton, however, usually contains somewhat less than this percentage, namely, about 13.3 per cent, owing probably to the presence of small quantities of one of the lower nitrates, the formula of which has already been given.

Generally speaking, the lower nitrates are soluble in a mixture of ether and alcohol, while gun-cotton is not dissolved by this liquid.

Gun-cotton requires a lower temperature than gunpowder for its ignition. The rate at which it burns depends on the mode of ignition and the conditions under which it is fired. A mass of loose gun-cotton may be ignited on the open hand without burning the skin or producing more than a momentary sensation of warmth, while the same cotton lightly twisted would produce a burn, and if confined in any sort of strong envelope would explode. The difference consists in the rate at which decomposition is transmitted through the mass, and the discovery that the explosion of a detonating fuse containing fulminate of mercury

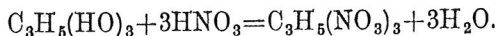
or some similar compound in contact with a mass of gun-cotton would cause it also to explode was a step of great practical importance.

Nitroglycerine, a compound similar in constitution to nitro-cellulose, both being nitrates, was discovered by Sobrero, an Italian chemist, in 1847. Though its explosive properties were known it was regarded as dangerous, and was not generally used as a blasting agent till after 1867 when Alfred Nobel discovered a method of rendering it portable and less dangerous by incorporating the liquid with a sufficient quantity of a fine silicious earth, called kieselguhr. The product is dynamite, which is familiar enough by name to the public.

Nitroglycerine is produced very simply by the interaction of a mixture of nitric and sulphuric acid with pure glycerine.

Glycerine is the secondary product obtained in boiling fat or oil with caustic alkali for the purpose of producing soap. But a large quantity is also produced by distilling fats in super-heated steam, when the fatty acid and glycerine are obtained, and it is only necessary to evaporate the watery part of the distillate to obtain the glycerine.

Glycerine, or glycerol as it is called in systematic chemical language, is a familiar colourless syrupy liquid, with a sweet taste. When mixed with nitric acid under suitable conditions it is converted into nitroglycerine, more correctly called glyceryl nitrate, and at the same time water is produced :



While formerly only small quantities at one time of glycerine were acted on by the acids, a charge of 1400 lbs. of glycerine may be now used in one operation in the apparatus called a nitrator-separator. In the modern practice a mixture of strong nitric acid and sulphuric acid is used, together with a certain amount of anhydrous sulphuric acid in the form of what is called *oleum*, which combines with a larger proportion of water, with the result that the yield of nitroglycerine is not far short of the theoretically possible amount. From the formulæ 100 parts of glycerine should yield 246.7 parts of the nitrate, while in practice upwards of 230 parts are obtained.

The nitrator-separator is a cylindrical leaden vessel with a coned top; inside are pipes through which compressed air is blown to mix the contents. The glycerine is introduced in the



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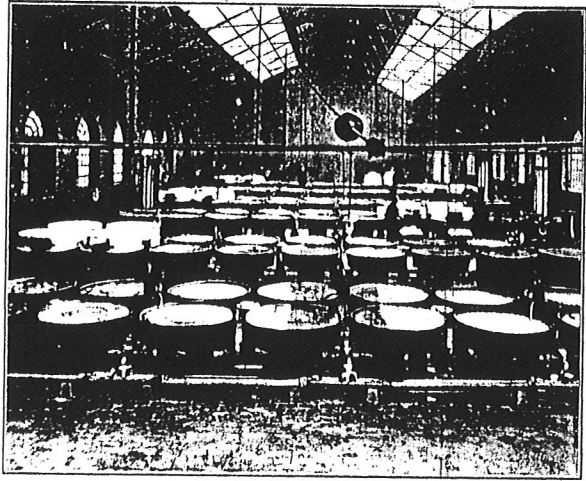


FIG. 122.—DISPLACEMENT PROCESS, WALTHAM ABBEY

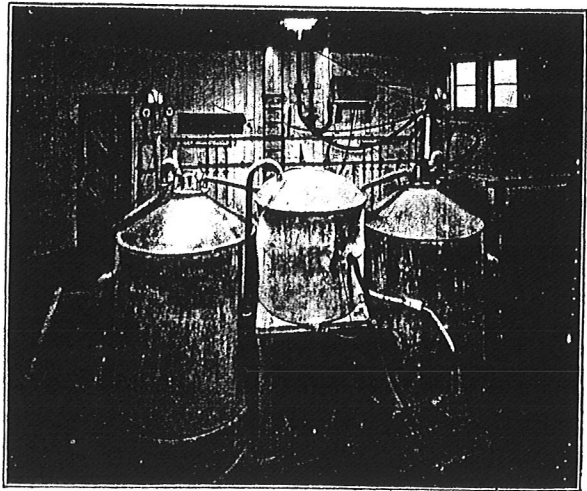


FIG. 123.—NITRATOR-SEPARATORS

form of a fine spray under the acid by means of a special injector worked also by compressed air. In order to avoid the possibility of accidents precautions are taken to see that the temperature does not rise beyond a certain point, generally  $28^{\circ}$  C. By reducing the flow of the glycerine and by increasing the agitation with the air any undue tendency to rise can usually be checked.

When everything goes right the nitration of the charge is usually completed in about one hour, the agitation with the air is discontinued, and the separation of the nitroglycerine from the acids takes place; being lighter it comes to the top. The nitroglycerine is forced out into a washing tank where it is stirred up repeatedly with fresh water, then with a solution of sodium carbonate, and finally with water. After this it is filtered to remove traces of water or impurities.

Nitroglycerine is a colourless oil of specific gravity 1.6, and therefore sinks in water in which it is insoluble. It has a sweetish taste and is poisonous. In minute doses it is used in medicine. When a lighted match is applied it burns quietly away, but it detonates violently when struck on an anvil by a hammer or by sudden heating to  $257^{\circ}$  C. Nitroglycerine becomes solid when exposed to frost, and in use it requires to be thawed, an operation attended by considerable risk. "Non-freeze" varieties of nitroglycerine are generally obtained by the addition of a small amount of the nitrate of a substance known as glycol, which is related to glycerine in composition.

In 1875 it was discovered by Alfred Nobel that when a low grade of gun-cotton and nitroglycerine are mixed together the cotton loses its fibrous or cellular structure, and becomes gelatinised. In the product each constituent has its explosive properties modified, and the mass becomes better suited to blasting purposes than either ingredient separately. This substance has been largely used under the name "blasting gelatine," and it is otherwise interesting as the forerunner of the various mixtures which have been the subject of experiment and which have resulted in the production of the chief military propellant *cordite*. It was discovered that not only could the lower nitro-celluloses be gelatinised by nitroglycerine, but that the most highly nitrated cotton could be blended with nitroglycerine if the mixture was treated with a common solvent such as acetone.

*gelatine*

To manufacture cordite the nitroglycerine is poured on to the gun-cotton contained in rubber bags and hand-mixed. The paste produced is then transferred to a large Pfeleiderer mixing machine, similar to the machine used in some bakeries for mixing dough, and the requisite quantity of acetone added. After working the mixer for some time, 5 per cent of vaseline is added to increase the stability of the product and lubricate the gun. When gelatinisation is complete the mass is pressed through a die of the requisite size, and the *cord* which is thus formed wound on a reel, or in the case of the thicker sizes it is cut into suitable lengths. The cordite is then dried slowly to drive off the last traces of acetone. In the case of the larger sticks, containing the smaller quantity of nitroglycerine, 30 per cent, this drying takes about two months.

The most important high explosives for use in shells are picric acid and trinitrotoluene, these are both obtained by acting on one or other of the constituents of coal-tar (see chapter XX, p. 308) with strong nitric acid.

In the manufacture of picric acid phenol, or carboic acid, is mixed first with about five times its weight of sulphuric acid when a compound known as phenol-sulphonic acid is formed. Strong nitric acid is then added gradually to the mixture, when trinitro-phenol, or picric acid, is produced in the form of lemon yellow crystals. The latter are removed and washed well to remove adherent nitric and sulphuric acids. Picric acid was at one time in common use as a dye for silk and wool, and is still employed medicinally for the treatment of burns. It melts at  $122^{\circ}.5$  C., and is a moderately strong acid, forming a variety of salts called picrates with metals.

Many of the picrates explode when heated or struck, but picric acid burns quietly. When the fused acid is supplied with a detonator it explodes violently, and it has been largely used under the name lyddite, or melinite, for charging shells. Experience has shown that lyddite shells are, however, somewhat erratic.

Trinitrotoluene, T.N.T., is found to be more trustworthy, and though its explosive force is somewhat less than that of picric acid it is preferred on account of its stability, and being not an acid but perfectly neutral it is not liable to attack the surface of metals.

Toluene is a colourless liquid which by the action of

strong nitric acid is converted successively into three nitro-compounds :

$C_7H_8$	toluene
$C_7H_7NO_2$	mononitrotoluene
$C_7H_6(NO_2)_2$	dinitrotoluene
$C_7H_5(NO_2)_3$	trinitrotoluene or T.N.T.

The toluene is first nitrated to produce mononitrotoluene ; this and strong sulphuric acid are then fed in at opposite ends of a series of pots, nitric acid being added at intermediate stages. The completely nitrated T.N.T. issues as an oil at one end of the series and spent acid at the other. The liquid T.N.T. is allowed to solidify on cooling and is then purified, generally by washing it with a solution of sodium sulphite which dissolves out most of the impurities.

Trinitrotoluene is a yellowish crystalline powder with a melting point about  $80^\circ C$ . When detonated by mercuric fulminate it explodes with great violence giving a quantity of black smoke, whence some of the names—Black Maria or Coal Box—given by the soldiers to shells of this kind.

T.N.T. is sometimes mixed with other substances, especially with an oxidising compound such as ammonium nitrate, together with a little aluminium powder and a trace of charcoal, the mixture being known as ammonal.

Other constituents of coal-tar yield explosive compounds under the action of nitric acid.

Dinitrobenzene, for example, enters into the composition of the mining explosives roburite and bellite. Trinitrocresol has been used in place of picric acid under the name ecrasite, but it shares the disadvantages of picric acid.

Cheddite is a name given to a permitted explosive containing potassium chlorate mixed with mononitronaphthalene, dinitrotoluene, and a little castor oil. Another variety of cheddite contains ammonium perchlorate.

One of the most powerful explosives known is tetranitroaniline, and a similar compound tetranitromethyl-aniline, known as "tetryl," is already used for detonators in place of mercuric fulminate. Another compound which has recently found application as a detonator is lead hydrazoate or azide,  $PbN_6$ , derived from hydrazoic acid or azoimide  $HN_3$ . The acid itself when in the pure anhydrous state and some of its organic

derivatives are among the most dangerously explosible compounds known, as they sometimes explode violently without obvious cause. But several of the metallic salts, such as the lead salt mentioned above, and the barium salt, are fairly stable and can be manipulated without risk, if proper precautions are taken.

A new explosive, which is said to exceed in power all others and has a remarkable rate of detonation, is known as "cyclonite" or "hexogen"; it is made by the action of nitric acid on hexamethylene tetramine, the product of the reaction between formaldehyde and ammonia (p. 338). The substance has the chemical name of cyclo-trimethylene-trinitramine, and it has been suggested for use as an initiating explosive.

In blasting operations gunpowder and detonators are fired by a time fuse or electrically. The time fuse is a case containing gunpowder which is made to burn at a known rate, generally 2 feet per minute. The instantancous fuse which burns at the rate of 100 to 300 feet per second affords the means of firing many charges simultaneously.

Enough has now been written to show the reader the general character of the chemical mixtures and compounds employed for military and naval use and for the peaceful purposes of the miner. But the subject is a very extensive one, and those who desire more technical information can best be advised to read the article on Explosives in Thorpe's *Dictionary of Applied Chemistry*.

An interesting application of explosives to the purposes of agriculture has attracted some attention during recent years, especially on the other side of the Atlantic. In new countries land has often to be cleared of wood and sometimes of masses of rock before it can be brought into cultivation. In order to get rid of trees it has been the custom in past times to burn them and leave the stumps to rot, before attempting their removal. This necessarily occupies a good many years, and the work is difficult and laborious.

As soon as modern explosives became available the idea of blowing up such obstructions naturally arose and has been put into operation on a considerable scale. But latterly the use of dynamite has been resorted to for the purpose of preparing holes for planting fruit trees and for loosening the soil between trees in orchards. As with every newly introduced practice there has been evidence of some degree of exaggeration in the reports

which have appeared in the press concerning the advantages of soil explosions.

The phenomena of combustion and explosion in gases have an interest both for the scientific man and for the coal miner, exposed as he is in the majority of pits to imminent risk in his daily work.

During the last sixty years great advances have been made in the theory of gaseous explosion, and in the knowledge of the rate of transmission of an explosion wave. The first steps in this direction were taken by the famous French chemist, M. Berthelot. At the time of the siege of Paris in 1870, Berthelot, then Professor in the Collège de France, became President of the Scientific Committee of National Defence. The superintendence of the manufacture of explosives to be used against the enemy naturally led him, after the war, to turn his attention to the systematic investigation of the phenomena of explosions. In the result he was able to connect the maximum velocity of the flame in a mixture of gases with the mean velocity of the molecules, according to the kinetic theory of gases. A long series of researches on the propagation of flame through mixtures of gases and on cognate subjects was begun by Messieurs Mallard and Le Chatelier in 1879, and the work of these distinguished French investigators is still frequently referred to. Work on this subject is still being carried on in England and in other countries, because of its importance in connection with the avoidance of explosions in coal mines.

A very important discovery was made in 1880 by the late Mr. Harold B. Dixon, then Professor of Chemistry in the University of Manchester. Dixon found that carbon monoxide mixed with oxygen, when dried as perfectly as possible, by long contact with phosphoric oxide, does not explode when an electric spark is passed through the gas. The admission of a minute trace of water vapour at once restores to the mixture its inflammability. Similar observations were made by the late Professor H. Brereton Baker, until recently Director of the Department of Chemistry in the Imperial College of Science and Technology, South Kensington. Dr. Baker's experiments showed that carbon, sulphur, and even phosphorus, when carefully dried, refuse to burn in oxygen when heated above the temperature at which they usually ignite. He also found that ammonia mixed with hydrogen chloride, and nitric oxide with oxygen are

indifferent when the gases are well dried. These results have been the subject of much speculation, but it is still not known definitely why quite small traces of water vapour are able to bring about reactions which do not take place in the perfectly dry gases.

Notwithstanding the greatly increased knowledge in our time about the properties of inflammable gases and of the conditions prevailing in coal pits, it is, unhappily, true that disastrous explosions continue to occur, in which many lives are lost, as they were before the invention of the safety lamp, in 1817, by Sir Humphry Davy. This fact is, of course, no ground for argument against the utility of the safety lamp.

The explosions which occur are due either to abuse of the lamp, to gross neglect of rules by miners, to blown-out shots, or some other cause. Among the sources of danger not recognised a few years ago is the accumulation of fine coal-dust in many workings.

Attention was first called to the subject by Mr. William Galloway so long ago as 1876, and much discussion and experimentation has been carried on since that time. The presence of fine coal-dust suspended in the air of a mine has long been known to add to the danger of explosions when they occur from presence of fire-damp; but it has only been recognised within recent years that dust alone, diffused through air, forms an explosive mixture through which flame is propagated, when once started, with the violence characteristic of gas explosion.

The English experiments, which form part of a comprehensive scheme for the investigation of the factors liable to cause explosions in coal mines, were at one time carried out at Altofts in Cumberland, but the work has now been transferred to the new Safety in Mines Research Board Experimental Station near Buxton, Derbyshire. The observations on dust explosions are generally carried out in a long iron gallery, made by bolting together a number of cylindrical iron boilers. In this gallery it is possible to cause dust explosions extending over several hundred feet, and the propagation of the flame and the pressure variations can be studied by means of instruments inserted at regular intervals. The work carried out under the direction of Professor R. V. Wheeler, Professor of Fuel Technology in the University of Sheffield, has shown definitely that dust explosions do not depend on the production of gas from the dust by a preliminary process

of distillation; an explosion can even be propagated through a cloud of charcoal in air.

The fact thus established is consistent with what is known of other dust explosions, as in flour mills, where there can be no question of the existence of inflammable gas in the atmosphere.

It has been found that by the admixture of sufficient stone dust to finely powdered coal the danger of inflammability is greatly diminished, and the Mining Acts of Great Britain make stone-dusting compulsory in order to diminish the danger of coal dust explosions. There is no doubt that this development, resulting from purely scientific studies, has resulted in the saving of many lives.

With the object of limiting the risk of explosions in coal mines, whether originating from gas or dust, the explosives to be used in fiery or dusty mines have to pass a Government test. A testing gallery has been erected at the Buxton research station, and there the effects of various explosives on an explosive mixture of gas, coal dust, and air are carried out. No explosive is passed for use in coal mines until it answers certain tests which indicate that it is reasonably safe.

Strictly speaking, there is no such thing as a perfectly safe explosive; under certain unfavourable conditions they will all ignite gas or coal-dust, but the "permitted test" does enable the various explosives to be sorted into grades of safety, and only those which have shown themselves to be the safest are allowed to be used.

The "safety" or "permitted" explosives in common use in British coal mines consist of an explosive substance, generally nitroglycerine or T.N.T., mixed with a relatively large proportion of an inert salt, such as common salt (sodium chloride), borax or ammonium oxalate. The object of the salt is to act as a cooling material, thus preventing the temperature of the explosion flame reaching that at which the coal dust-air and methane-air mixtures are likely to explode. Mixtures of 80 to 90 per cent of ammonium nitrate, together with T.N.T. or nitroglycerine are also used for the same purpose.

A new development in connection with safety explosives is the use of the so-called Cardox cartridges, which contain liquid carbon dioxide under pressure. They are set off by passing an electric current through a mixture of two substances, such as a phenolic product and potassium chlorate, which generate a large

CARDIX



amount of heat when they combine chemically. This heat causes the liquid carbon dioxide to evaporate rapidly, and the volume of gas is so large that the process takes place with explosive violence. Since no flame is produced during the explosion there is no danger of setting off the explosive mixtures present in the atmosphere of a coal mine.

## CHAPTER XXVII

## FIXATION OF ATMOSPHERIC NITROGEN

At the meeting of the British Association for the Advancement of Science held at Bristol in 1898, Sir William Crookes in his address as president drew attention to what he called the "Wheat Problem." In the course of his discussion of the facts he produced something approaching a serious sensation by the statement that "England and all civilised nations stand in deadly peril of not having enough to eat. As mouths multiply, food resources dwindle. Land is a limited quantity, and the land that will grow wheat is absolutely dependent on difficult and capricious natural phenomena."

It is true that he added to this alarming view, "I hope to point a way out of the colossal dilemma. It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty."

Fortunately for public peace of mind some relief from anxiety was provided a few months later in a letter addressed to *The Times* on December 2nd, 1898, by Sir John Bennett Lawes and Sir J. Henry Gilbert, the famous experimental agriculturists of Rothamsted, England. They said: "To sum up the world's wheat supply it may be said that whilst wheat is capable of producing very large crops under favourable conditions as to soil, climate, and manuring, it possesses a remarkable power of obtaining food from a poor soil. It can stand a considerable amount of frost, and it can thrive over an immense area of the world's surface. Although endorsing all that Sir William Crookes says as to the importance of wheat as a food, we cannot adopt his desponding views in regard to the future supplies of it.