

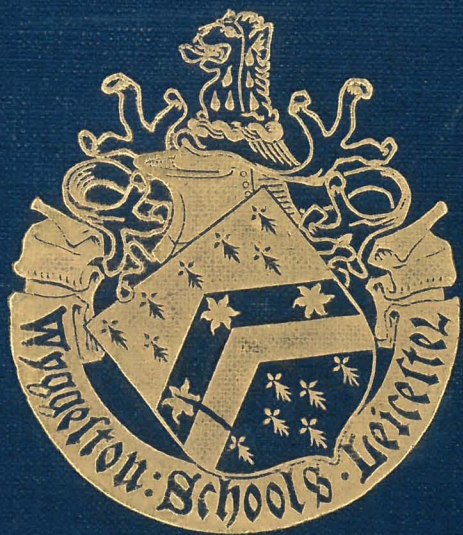
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CHEMICAL
DISCOVERY
& INVENTION
IN THE
TWENTIETH
CENTURY

TILDEN


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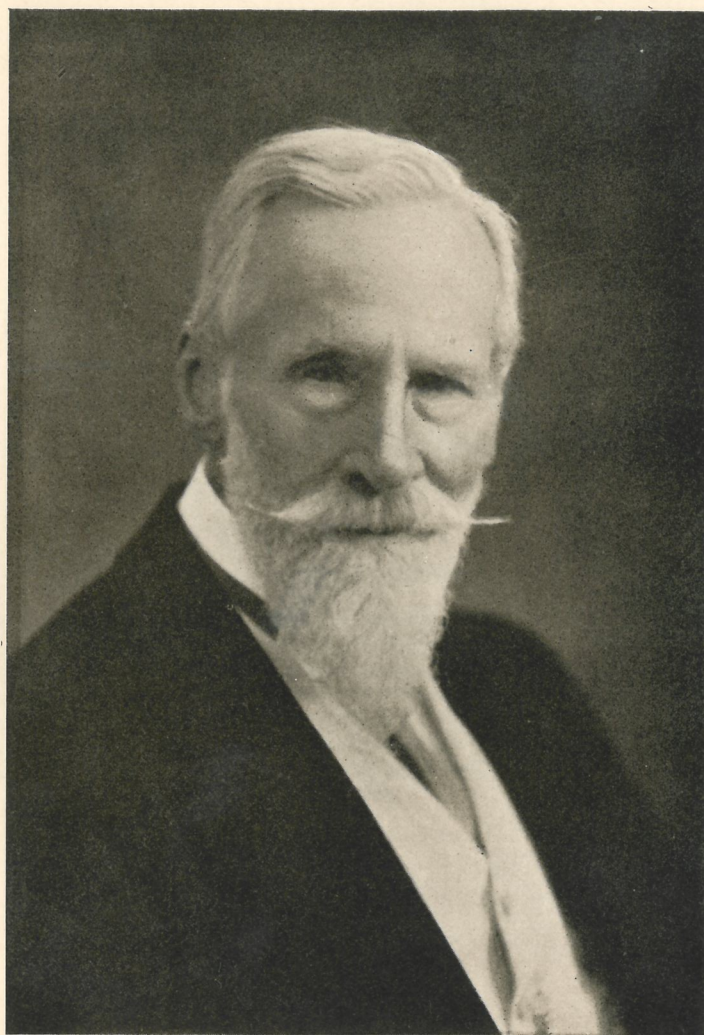
July, 1923.

Brewer, A.

Form *VI* Science

Senior Mathematics Prize

T. Kingdom M.A.
Head Master.



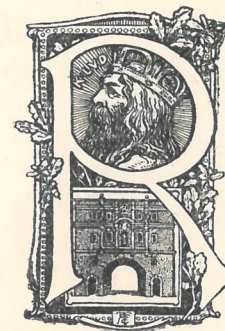
William Crookes.

Frontispiece.

CHEMICAL DISCOVERY
AND INVENTION
IN THE
TWENTIETH CENTURY

BY
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"For we are borne to quest and seeke after trueth ; to possesse
it belongs to a greater power."—FLORIO'S *Montaigne*.



LONDON
GEORGE ROUTLEDGE AND SONS, LIMITED
BROADWAY HOUSE, CARTER LANE, E.C.
NEW YORK: E. P. DUTTON AND CO.

First Edition published January, 1917
Second Edition (Revised) November, 1917
Third Edition (Revised) June, 1919

PREFACE

IN accepting the invitation of the publishers to write a book of a popular character on modern chemical discovery, I am conscious of undertaking a very serious task. The difficulties to be encountered are twofold; first, there is the complexity and diversity of the subjects to be dealt with, and, secondly, the difficulty of rendering an account of many of them in language at once intelligible to the non-technical reader and free from serious inaccuracy. The author is indebted for assistance from many friends, and in connection especially with the chapters dealing with manufacturing processes such help was indispensable. To all in the following list who have thus kindly given information or supplied illustrations he desires to return his most grateful thanks.

Professor S. Arrhenius, of Stockholm.
Professor A. J. Brown, of Birmingham.
Professor W. A. Bone, of the Imperial College.
The Council of the Chemical Society.
Sir William Crookes, President of the Royal Society.
Lt.-Col. Professor A. W. Crossley.
Sir James J. Dobbie, Chief Government Chemist.
C. S. Garland, Esq., of the Volker Lighting Company.
J. C. Maxwell Garnett, Esq., Principal of the Municipal School of Technology, Manchester.
The Gas Light and Coke Company.
R. S. Giles, Esq., of Rangoon.
Messrs. Hird, Chambers, and Hammond, Chemical Engineers, Huddersfield.

anything previously known, as for example in paving the streets, and the extra demand would for a time at least tend to raise the price again. At any rate there seems no reason at the present stage of the researches which are going forward for rubber planters to entertain alarm. The change, if it came about, would not take place in a moment, and there would be ample time for the land now occupied with rubber trees to revert to its primitive use in the provision of food.

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 at the time of writing this book the greater part of Europe is devastated and millions of men are exposed to destruction by the wholesale use of explosives in 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 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 the group of atoms, NO_2 , 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 introduced, 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 of 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.¹

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.

Cotton consists of the hairs from the seed of the cotton plant (*Gossypium herbaceum* and other species, N.O. *Malvaceæ*). When looked at with a microscope they are seen to consist of long flattened twisted tubes of translucent substance. This

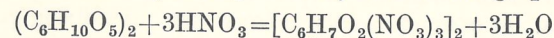
¹ The invention of gunpowder is by the English attributed to Roger Bacon, who was born in 1214. Others suppose a certain monk, of whom nothing positive is known, but who is supposed to have lived in the early part of the fourteenth century, to have been the inventor. He is commonly spoken of as Berthold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

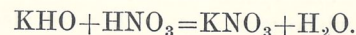
Those who are interested in the history of the subject should consult *Monumenta Pulveris Pyrii*, by the late Oscar Guttman, 1906.

substance is called *cellulose*, it has the composition expressed by the formula $(C_6H_{10}O_5)_n$, and it forms the fundamental material of vegetable tissues in general. Clean cotton consists of almost pure cellulose, and when ignited it burns away leaving only a minute quantity of mineral matter in the form of ash.

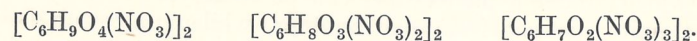
When cotton is immersed in strong nitric acid an interchange takes place which may be expressed by the following equation :—



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 :—



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 quantity in many 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.

The following account of the manufacture of gun-cotton is chiefly taken from a lecture given by Mr. William Macnab before the Institute of Chemistry of Great Britain and Ireland in February, 1914.

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. "The object of the restrictions is 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. 131), that in the event of an explosion the effect is localised as much as possible, and the explosives in the adjacent buildings are not 'set off.'" Special precautions are taken to prevent the accumulation of dusty explosive matter, and scrupulous cleanliness is enforced. No naked iron or steel is allowed where the more explosive materials are treated; the workers have to wear shoes containing no iron or steel nails; and in order to prevent the introduction of grit from the outside those entering the building temporarily have to slip on large shoes which are kept at each building specially for this purpose. Everyone on entering an explosive works has to give up any matches he may have in his possession; the work-people have to wear special outer clothing without pockets; and women have to fix their hair without pins which might possibly fall in among the explosives with which they are working.

The lighting of the buildings is nearly always electrical, and where motive power is required, it is usually supplied by electric motors placed outside the building.

It is not permissible to use a house for a different operation from that for which it is licensed without special authorisation. Serious penalties follow the breach of the terms of the licence under which the factory is allowed to work, and surprise visits from the Inspectors of Explosives help to maintain a good state of discipline.

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. 133) 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 1¼ 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 placed in an earthenware covered pot standing in water, and left for about twelve hours (Fig. 134). 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 by means of a machine similar in construction to the machines used by paper-makers. It is then in a very fine state of division, and, 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



FIG. 131.—MOUNDED HOUSE. COTTON POWDER WORKS.

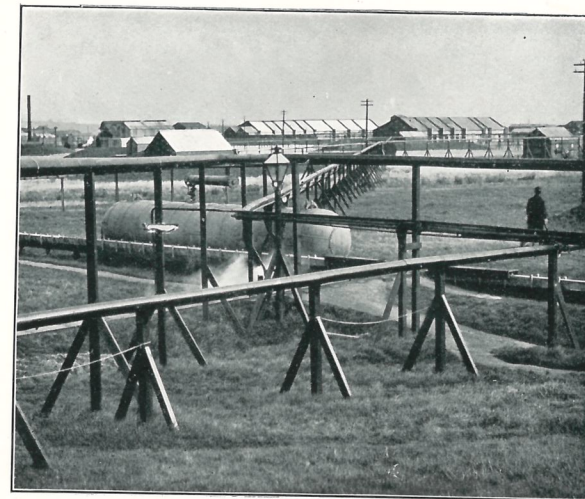


FIG. 132.—BUILDINGS AND PIPE CONNECTIONS. COTTON POWDER WORKS.

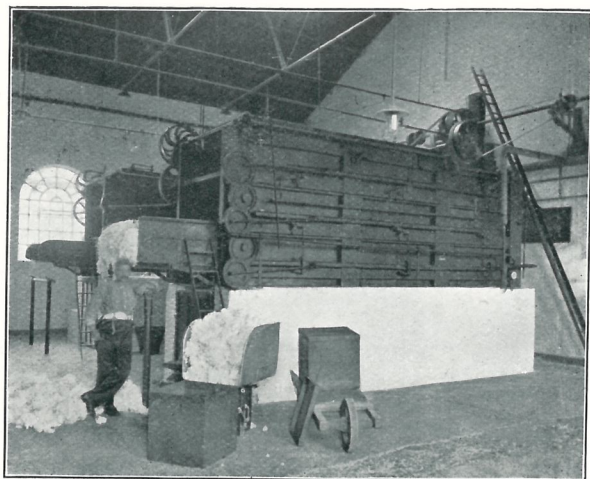


FIG. 133.—DRYING MACHINE. WALTHAM ABBEY.

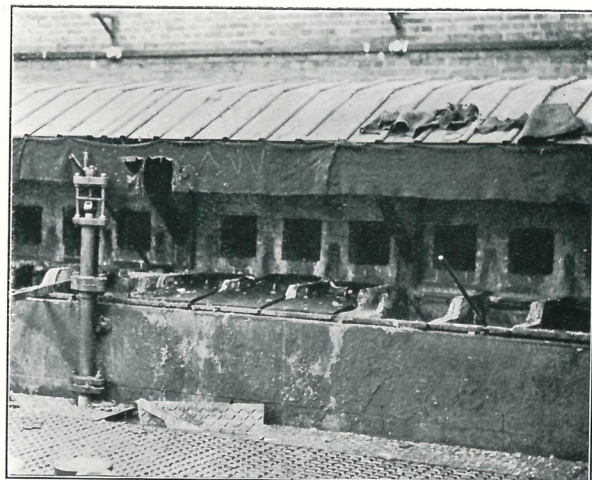


FIG. 134.—ABEL, NITRATION PROCESS. DIPPING PANS. WALTHAM ABBEY.

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 lb. of dry cotton.

Hoods connected with an exhaust fan draw off the fumes from the acids, and these hoods are made of aluminium, a metal which is practically unacted on by nitric acid. 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 of the acid. This prevents the escape of acid fumes and allows of the removal of the hoods. After two and a half hours the nitration is complete; the spent acid can be drawn off, and an 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.

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.

The solution of these lower nitrates in ether-alcohol constitutes "collodion." It must be remembered that cotton is not strictly speaking a definite chemical substance, and it varies somewhat in physical state, and hence that cottons from different sources, under the same conditions in a bath of the same composition, while yielding nitrocellulose containing the same percentage of nitrogen, may vary considerably in solubility. In the early days a high degree of nitration, say 12.8 per cent of nitrogen or upwards, was generally associated with insolubility in ether alcohol, while lower content of nitrogen corresponded with greater solubility. With greater experience, however, it is now possible to produce nitrocellulose with a high percentage of nitrogen and complete solubility in ether-alcohol.

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 nitrocellulose, 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 incor-

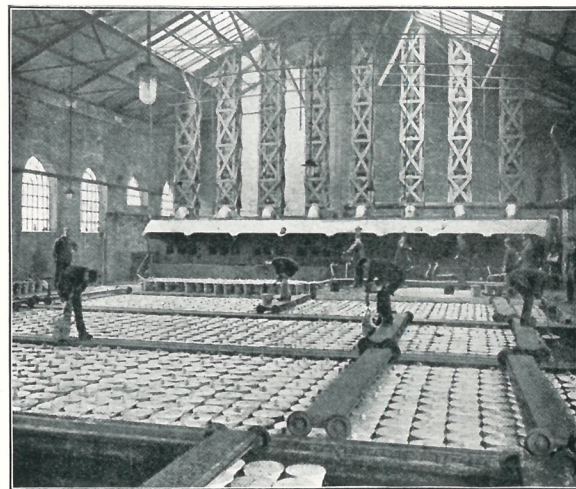


FIG. 135.—ABEL NITRATION PROCESS. WALTHAM ABBEY.

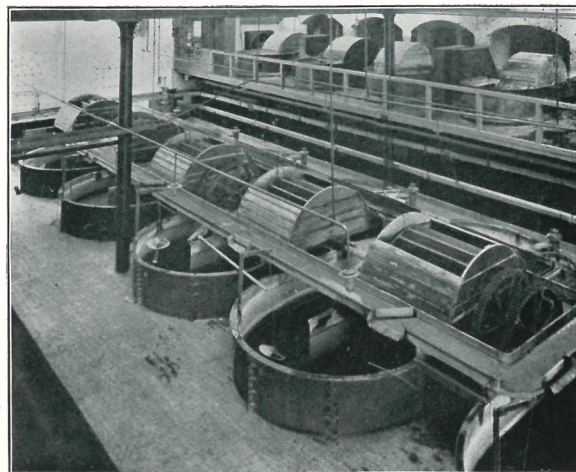


FIG. 136.—BEATING ENGINES AND POACHER. WALTHAM ABBEY.

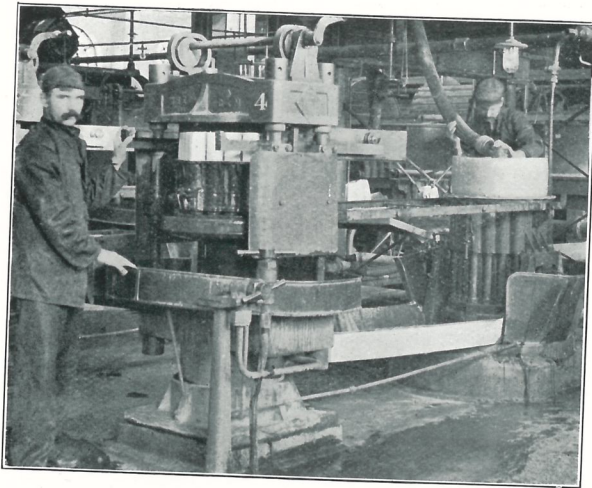


FIG. 137.—MOULDING MACHINE. WALTHAM ABBEY.

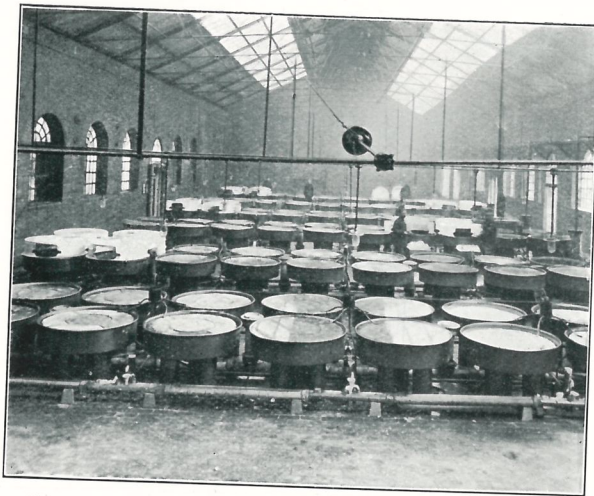


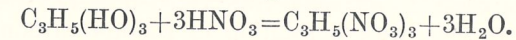
FIG. 138.—DISPLACEMENT PROCESS. WALTHAM ABBEY

porating 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. It mixes with water in all proportions, and when mixed with nitric acid it is converted into the nitrate, or nitroglycerine, at the same time that 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 with sulphuric acid is used, to which is added 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 placed leaden coils, through which cooling water circulates, and pipes through which compressed air is blown to mix the contents. The glycerine is introduced in the form of a fine spray under the acid by means of a special injector worked also by compressed air. Long thermometers passing through the top of the nitrator-separator enable the temperature to be watched, and it is the business of the man in charge of the operation to see that the temperature does not rise beyond a certain point, generally 28° 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.

"Should, however, the temperature continue to rise and pass the danger mark then a large cock in the bottom of the nitrator is opened, and the contents are rapidly discharged into a large tank, containing water, outside the building, where the charge is 'drowned,' and thereby the danger avoided of serious decomposition and probable explosion.

"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. A pipe in which a glass window is fitted leads from the top of the nitrator-separator to a pre-washing tank; by allowing waste acid from a previous operation to enter at the bottom the nitroglycerine is forced over into the washing tank, and the flow of acid is stopped whenever all the nitroglycerine has passed into the washing tank, which can be observed through the window." In the washing tank the nitroglycerine 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° C. Nitroglycerine becomes solid when exposed to frost and in use it requires to be thawed, an operation attended by considerable risk.

When nitroglycerine is exploded it yields a mixture of carbon dioxide and nitrogen with 4 per cent of free oxygen, whereas when nitrocellulose is fired the carbon dioxide and nitrogen are accompanied by carbon monoxide and a considerable quantity of free hydrogen. In the latter case the relative proportions of these gases vary with the pressure developed in the space in which explosion occurs. It appears that even when oxygen is present in excess, oxides of nitrogen are never formed in a normal explosion. Nitrous fumes are however formed when one of these high explosives burns freely without explosion.

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 gela-

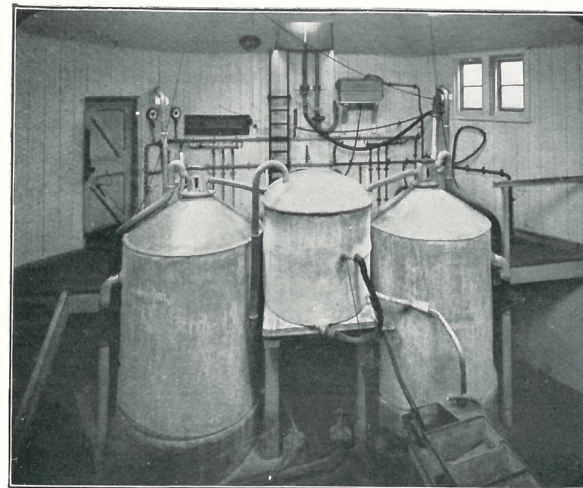


FIG. 139.—NITRATOR-SEPARATORS.

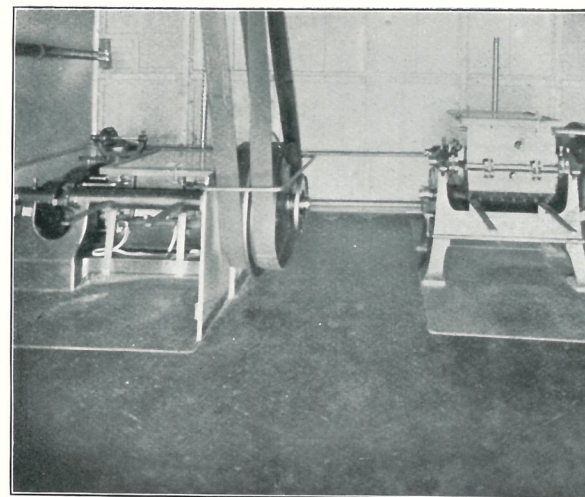


FIG. 140.—CORDITE MIXING MACHINE.

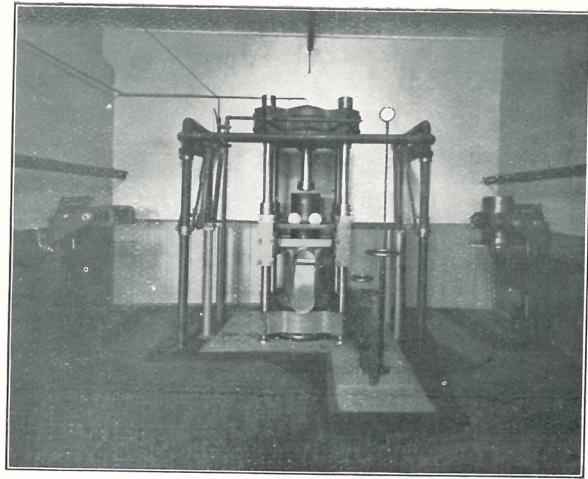


FIG. 141.—CORDITE PRESS.

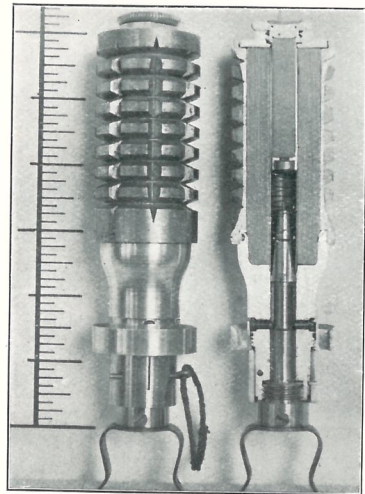


FIG. 142.—MARTIN HALE'S GRENADE.

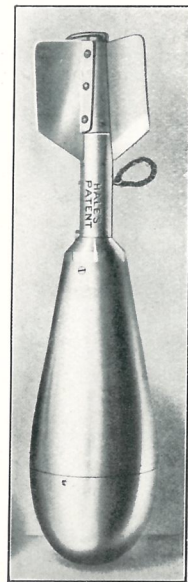
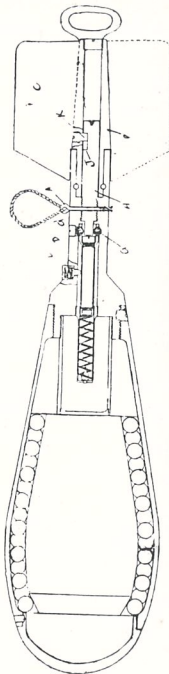


FIG. 143.—MARTIN HALE'S BOMB.



tinised. 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.

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.

It is interesting, says Mr. Macnab, to note the accuracy which has been attained in this manufacture. For rifles, for instance, the velocity prescribed is 2380 foot seconds, with a *plus* or *minus* of only 40 feet, and a pressure of 19.5 tons, with a maximum of 20 tons per square inch; for larger guns it may be 2500 foot seconds + 15 foot seconds, and the pressure must not exceed 19 tons per square inch.

In July last (1915) Professor Vivian Lewes¹ of the Royal Naval College, Greenwich, in some lectures delivered before the Royal Society of Arts gave some interesting facts concerning the explosives used in the European war, from which the following condensed account is taken. The shells used in big guns and field artillery may be divided into two main classes, namely shrapnel and high explosive shells. The shrapnel shell, named after its inventor, is a hollow cylindrical projectile packed with

¹ Professor Lewes, unfortunately, died on October 23rd, 1915.

bullets, at the base of which is a bursting charge, which may be gunpowder or a high explosive, while in the nose of the shell is arranged the time fuse connected by a tube with the bursting charge. This can be so regulated that the shell bursts in the air at any desired point. Shrapnel, however effective against troops in the field, does but little damage to earth works, wire entanglements, and other defences. Hence for the latter purpose high explosive shells are required. These consist of forged steel with comparatively thin walls and a heavy bursting charge. The explosive with which such shells are charged is usually one of the products of nitration obtained by acting on one or other of the constituents of coal-tar (see Chapter XX, p. 310) with strong nitric acid.

Phenol or carboic acid mixed first with an equal weight of strong sulphuric acid and the compound introduced gradually into three times its weight of strong nitric acid gives trinitrophenol or picric acid. This is a lemon yellow crystalline substance which has long been used as a dye for silk and wool. It melts at $122^{\circ}\cdot 5$ C., and is a moderately strong acid, forming a variety of salts with bases.

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 in the South African War showed 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.

Trinitrotoluene is a yellowish crystalline powder with a melting point about 79° 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.

Probably the most powerful explosive known is tetranitroaniline, and another 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 triazide, 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.

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 instantaneous fuse which burns at the rate of 100 to 300 feet per second affords the means of firing many charges simultaneously.

Of the bombs which have come into use in warfare with the development of airships and aeroplanes there are several varieties. The British air service during the war is understood to have made use of the bomb designed by Marten Hale, Fig. 143. This is an ingenious arrangement which has the great advantage that it can be handled and transported quite safely. In the neck of the bomb is a propeller which, when free and falling through the air,

spins round and releases the detonator so that on impact it flies forward into the bursting charge and strikes a firing needle which causes the explosion of the bomb. Before being dropped a pin which holds the vanes is withdrawn and a fall of 200 feet suffices to set the vanes spinning as described.

The incendiary bombs used by the Germans consist of a shell wound round with tarred rope and containing a quantity of resin and other inflammable matter, in the midst of which is a charge of "thermit" (p. 262) with usually a quantity of red phosphorus at the bottom. In thermit advantage is taken of the very high temperature produced by the combination of metallic aluminium with oxygen. A mixture of fine powder of aluminium with oxide of iron was introduced under this name about 1898 for the purpose of welding together steel rails, repairing castings, or heating iron bolts white hot. The mixture being packed round the object to be heated is ignited by means of a piece of magnesium ribbon which can be lighted by a match. The iron in the oxide is reduced to the metallic state and remains when the action is over as a fused mass.

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 only 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 very 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.

There can be no doubt that the aeration of the soil, the breaking up of the subsoil, especially when hard, the destruction of vermin, and the saving of labour are advantages generally recognised. The two questions in respect to soil improvement by explosion which must be considered are first whether it is effectual in all cases, and secondly does it pay? There seem on both these points to be as yet a lack of unanimity, which perhaps is due to want of experience, as the method is so new. The experiments on limes, bananas, and other crops in the West Indian Islands as reported in the *Agricultural News* published by the Imperial Department of Agriculture, Barbados (March 11, 1916), show that much further experience is necessary before a definite conclusion can be reached, as it appears that in these islands and for the crops referred to the results obtained have not been encouraging.

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 forty years great advances have been made in the theory of gaseous explosion, and in a 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.

Another very important discovery was made in 1880 by Mr. Harold B. Dixon, a few years later 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. This discovery has been very fruitful in the way of discussion, and a hypothesis put forward soon afterwards to the effect that chemical combination between two substances was impossible without the presence of a small quantity of a third substance met with a good deal of favour. This hypothesis seemed to be further supported by discoveries of a similar kind made a few years later by Dr. H. Brereton Baker, now Professor in the Imperial College of Science and Technology at 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. Whether in all cases a third substance is essential to the act of chemical combination must, however, be still regarded as an open question, notwithstanding the interesting suggestiveness of the experiments referred to. Much has yet to be learnt as to the constitution of gases and the real nature of chemical action, especially since the doctrine concerning electrons and their functions has become generally accepted (see pp. 118 and 212).

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.

In France and in England large scale experiments have been carried out within the last few years which have supplied very valuable information. The English experiments at Altofts have been provided for by the Mining Association of Great Britain, and have been described by Professor Dixon in his Presidential Address to the Chemical Society (London) in 1911 in the following passage:—

“An iron gallery 600 feet long and $7\frac{1}{2}$ feet in diameter was constructed of cylindrical boilers bolted together. Inside a tram-line on a concrete floor, with props and cross-timbers placed at 9 feet intervals, made a travelling road, comparable with the main haulage road of a mine. Shelves fastened to the sides provided ledges for holding dust, and the flame of a blown-out shot was reproduced by firing a stemmed gunpowder charge from a cannon. Just before firing a current of air was drawn into the main gallery by a fan placed at the end of a ‘return’ gallery. By this means a pure coal-dust explosion, extending over several hundreds of feet, could be obtained, and the propagation of the flame and pressure studied.”

The reports of the French Coal-Dust Experiments conducted at the Liévin Experimental Station, near Lens, in 1907–10, have been published in English by the *Colliery Guardian*. Experiments were made similar to those described, and with similar results. The principal gallery, constructed originally only 71 yards long, was extended till in 1910 it was 328 yards long, with an internal height of 6 feet.

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. The initiation of the flame does not apparently depend on the production of gas from the dust by a preliminary process of distillation, and Dr. R. V. Wheeler, who has been in charge of the laboratory at Altofts, has been able to show that an explosion is propagated through a cloud of *charcoal* dust in air.

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 by the Home Office at Rotherham, and there the effects of various explosives on an explosive mixture of gas and air are carried out. A charge is fired from a gun with a 2-inch bore, which represents a bore-hole, into the cylinder containing an explosive mixture of gas and air, or air in the presence of coal-dust laid along the cylinder. Shots are then fired electrically till the largest charge is found, which can be fired without igniting the mixture. Further shots are then fired till five shots of the same weight have been fired without igniting the mixture.

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 (Macnab).

In consequence of the extensive manufacture and use of explosives in modern times it has been necessary, in all civilised countries, to regulate by legislation the conditions under which they may be made, stored, and distributed. Many of the enactments are self-evident in their application: buildings for the factory must be licensed, stores in mines and quarries must be registered, explosives must be properly packed, and imports from abroad require special licences. Inspectors are also appointed whose business it is to make surprise visits for the purpose of observing that the regulations for the safety of workpeople and all the conditions of the licences are duly carried out.

Explosives of any new composition require to pass a strict examination before they are authorised, and all must be in a condition which indicates reasonable safety when kept and freedom from serious danger from friction or blows when packed or in transit.

Explosives differ considerably in stability, some being liable to slow decomposition which in course of time may assume a dangerous character. This is especially true of the nitric "esters," that is so-called nitrocelluloses and nitroglycerin, and more especially if the temperature is somewhat elevated as in tropical countries, in the holds of ships, and especially in positions where the temperature may be raised in consequence of the position of

boilers, or of cargo like coal, which may undergo chemical change and therefore possible spontaneous heating.

When nitrocellulose commences to decompose from the presence of minute traces of acid, a mixture of oxides of nitrogen is given off among which nitrogen peroxide is recognisable by its orange-brown colour. A test therefore is based on the heating of the material in a long narrow test tube to 135° C. and noting the lapse of time before the first faint yellow colour is seen in the air contained in the tube. A more delicate test consists in heating in a closed test tube a quantity of the cotton to a prescribed temperature, while a piece of paper impregnated with a mixture of starch with an iodide and moistened at the end with glycerine is suspended in the tube. The number of minutes which elapses before the paper becomes discoloured serves to indicate the quality of the explosive according to its class.

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