Nathan FL

Nitroglycerine and its Manufacture

Journal of the Society of Chemical Industry 1908

to handle from a clarified solution than from one that has received no treatment. On the other hand, it may be pointed out that if, as is frequently the case, a considerable excess of lead is employed to effect clarification, unless great care is exercised to effect its complete removal from the clarified solution, it is liable to give rise to large errors in Fehling determinations performed with the clarified solutions. In the past it has always been our practice to carry out the volumetric determination on the untreated solution in accordance with British practice.

In conclusion we would state that it is not our intention to suggest that such a high degree of accuracy is obtainable by means of the volumetric process as with the gravimetric methods. In our opinion, however, very material improvements can be effected in it on the lines we have indicated so as to render it sufficiently accurate for all ordinary technical analytical purposes, but where great accuracy is desired the preference should undoubtedly be given to the gravimetric method.

Discussion.

Mr. A. R. **Ling** said that the use of acidified ferrocyanide solution as indicator, in conjunction with folded filter paper, was well known. He had come to the conclusio hat ferrocyanide solution in any form was not suffic y sensitive, and had given it up in favour of the indicator, ferrous thiocyanate, which was described in a paper read by Mr. Rendle and himself before the Society of Public Analysts in 1905 (this J., 1905, 753), and which the authors had not referred to, possibly because they had not seen it. In that paper it was shown that the titration of solutions of invert sugar, dextrose, and maltose could be carried out with ease to 0·1 c.c., a degree of delicacy which could never be obtained when ferrocyanide was used as an indicator. He presumed that the authors in giving a constant for the influence of cane sugar were only dealing with mixtures ontaining very small proportions of invert sugar and arge proportions of cane sugar.

Mr. A. C. **Chapman**, referring to the filter paper method ecommended by the authors for applying the ferroyanide test, said he was rather surprised that no reference ad been made to the thiocyanate (sulphocyanide) indiator; he felt that sugar chemists generally were very nuch indebted to Mr. Ling for having brought this ndicator to their notice, since it was certainly much uperior to the ferrocyanide, and had done a great deal o increase the accuracy of the volumetric method.

Mr. E. G. **Hooper** said he thought that no sugar hemist was likely to need to keep Fehling's solution for 4 months. From his experience of many years' working vith this solution, he found that within a period of 3 or weeks there was no appreciable variation, the solution, f cou being kept in a shaded place. The method f app. g the indicator referred to appeared unnecesarily elaborate. His own practice had been to fold a wedish paper thrice, drop the solution on the upper de, and apply the test to the under portion which, on nfolding the paper, occupied the middle of the filter; had found that perfectly satisfactory. He should have een inclined to expect—though he had no experience anything beyond English summer temperatures—at Fehling's solution would deteriorate more rapidly—referred of course to the complete, mixed solution—a hot climate than in cool regions, but if such deterioraon were found to be serious, there seemed to be no eat advantage in the mixed solution, and the remedy as of course to be found in keeping the copper solution d the alkaline solution apart, only mixing when actually quired.

Dr. E. **Divers** said that it was well known that Fehling's lution in the dark kept well for a long time, and that soon altered in a strong light. It was not the best actice to test the filtrate after passing very little of it rough several folds of paper, because of adsorption copper salt by cellulose.

Mr. J. L. **Baker** said he should like to make it clear at the authors were not in the habit of keeping their aline tartrate and copper sulphate solutions mixed 14 months, but this was an experiment to show what change would take place if the mixed solution was kept for that unusual period. He could imagine, however, that for chemists who were working under great pressure during a sugar campaign, it would be a very decided advantage if they could prepare a large quantity of mixed solution ready for testing. Anyone who had worked in sugar factories would appreciate the force of that remark.

Mr. **Grant Hooper** said he had made up to 10 litres at a time, and kept them over 3 weeks without any appreciable change.

Meeting held at Burlington House on Monday, February 3, 1908.

DR. J. LEWKOWITSCH IN THE CHAIR.

NITROGLYCERINE AND ITS MANUFACTURE.

BY LT.-COL. SIR F. L. NATHAN, R.A., AND W. RINTOUL, F.I.C.

The Memoirs of the Royal Academy of Science of Turin, published on Feb. 21, 1847, contains a paper by Professor Ascanio Sobrero, entitled "Concerning some new explosive compounds obtained by means of the action of nitric acid on organic vegetable substances." The first portion of the paper summarises the work published by him in the previous year on nitromannite, &c., and he then proceeds as follows:—"The oxidability of glycerine is very great; nitric acid reacts violently upon it and produces oxalic acid, although it would seem probable that this is only the ultimate degree of oxidation to which it attains through intermediate stages corresponding to more complicated substances. However that may be, when concentrated nitric acid, or a mixture of two volumes of sulphuric acid at 66° B., and one volume of nitric acid at 43° B., is added to glycerine concentrated to the consistency of a thick syrup, oxidation takes place immediately and tumultuously, producing copious nitrous fumes. I have had no opportunity of studying the products of this oxidation. If, however, instead of pouring the acid mixture into the glycerine, the operation is reversed, taking the precaution of keeping the acids in a freezing mixture at a temperature several degrees below zero, a different reaction occurs. The glycerine dissolves when it comes in contact with the acids, the solution being facilitated by shaking the containing vessel. When solution has been effected, the liquid is quickly poured into distilled water at ordinary temperature, and immediately a considerable quantity of liquid drops are precipitated at the bottom of the vessel. These drops unite and form a layer, which, if undisturbed, separates completely from the water. These drops constitute the new substance whose properties I am about to describe, and which I will call piroglycerine." Sobrero found that piroglycerine possessed "detonating power to a high degree," but no use was made of it as an explosive for many years after its discovery by him.

It has been stated that mines or torpedoes charged with nitroglycerine were employed during the Crimean War to protect the water approaches to the fortress of Cronstadt, and that their supposed existence deterred the British fleet from entering the harbour. There does not appear, however, to be any accounts of these mines having produced explosive effects.

In 1863, Alfred Nobel introduced piroglycerine, which he called nitroglycerine, as a blasting agent, in Norway. It was first of all employed in the liquid state and was exploded by means of small charges of gunpowder, or detonated by means of percussion caps containing fulminate of mercury (Eng. Pat. 1813 of July 20, 1864). Its use now spread rapidly, but many accidents occurred with it, and, in consequence, its employment was prohibited by many governments. To render liquid nitroglycerine safe for purposes of transport, Nobel dissolved it in various solvents, but in order to use it, it had to be separated from these solvents, so that nitroglycerine treated in this way was not a success.

Pure nitroglycerine freezes easily at about 8° C., and in the frozen condition it is much safer to transport. This property was made use of in America by G. M. Mowbray, who, in 1868, erected a factory for the manufacture of nitroglycerine for use in the construction of the Hoosac tunnel, Massachusetts. Large quantities of nitroglycerine were made at this factory, and successfully employed in the blasting operations in connection with this tunnel, and other works. It was transported all over America in a frozen condition without apparently any serious accidents, and the use of frozen nitroglycerine was continued in America for many years.

Meanwhile Nobel, after a long series of experiments, commencing probably about 1863, when he took out a patent for mixing nitroglycerine with ordinary gunpowder, sodium nitrate, or a mixture of carbon and sulphur (Eng. Pat. 2359 of Sept. 24, 1863), succeeded in finding a substance which would absorb very large quantities of nitroglycerine, and in this way he got rid of the difficulties and dangers incidental on the use of liquid nitroglycerine. The material he employed was kieselguhr, an infusorial earth, and to the product he gave the name of "dynamite" (Eng. Pat. 1345 of May 7, 1867). Nobel eventually succeeded in replacing the kieselguhr by an explosive absorbent, and in 1875 he patented "blasting gelatine," the most powerful form of which consists of 93 parts by weight of nitroglycerine, and 7 parts by weight of soluble nitrated cellulose (gelatinised) (Eng. Pat. 4179 of Dec. 2, 1875).

Both dynamite and blasting gelatine are explosives suitable only for blasting or disruptive purposes. By considerably reducing the proportion of nitroglycerine whilst increasing that of the soluble nitrated cellulose, Nobel produced an explosive for propulsive purposes; this he patented in 1888 under the name of "ballistite" (Eng. Pat. 1471 of Jan. 31, 1888). Meanwhile, the Explosives Committee in England were working on the production of a smokeless propellant in which nitroglycerine was combined with guncotton or insoluble nitrocellulose, in place of the soluble nitrocellulose used by Nobel, and in 1890 they patented "cordite" (Eng. Pat. 11,664 of May 24, 1890).

Nitroglycerine is now used as a constituent of a large number of both disruptive and propulsive explosives.

Early Manufacture.—In the early days of the manufacture of nitroglycerine, only small quantities were produced at one operation, and the apparatus employed was of the simplest description. It consisted usually of a pot of cast iron, china, or lead, in which the nitration was carried out. The pot contained the mixed acids and was stood in an outer vessel full of cold water. The glycerine was poured very slowly from another vessel into the mixed acids, and whilst it was running in the contents of the nitrating pot were kept well stirred by hand. When all the glycerine had been added, the nitroglycerine formed was allowed to settle out from the waste acid in a separating funnel and then run into water and washed. The washing was generally very imperfect, and the nitroglycerine so made was obviously not suitable for prolonged storage. The quantity of nitroglycerine produced in one operation only amounted to, say, 100 grms., and when fairly large quantities came to be required, the number and size of nitrating pots was increased, mechanical arrangements for regulating the inflow of glycerine and for agitation during nitration were introduced, and greater care was taken in the preparation of the nitrating acids and in purifying the nitroglycerine.

The most successful, probably, of the early factories for the manufacture of nitroglycerine on a commercial scale, was the one at North Adams, Mass., erected by G. M. Mowbray in 1868. Compressed air was used for thoroughly mixing the acids and removing nitrous fumes. The nitrating vessels were stone pitchers to the number of 116, they stood in wooden troughs filled with ice-cold water, or ice and salt. The charge of mixed acid was 17 lb. The glycerine, contained in glass jars placed at a higher level, syphoned over drop by drop into the mixed acid, and the contents of the nitrating vessel were kept agitated during the inflow of the glycerine by means of compressed air led in through a glass tube. The nitration lasted 1½ to 2 hours. Temperatures were taken frequently during nitration, and if a rise took place or nitrous fumes were given off, the inflow of glycerine was reduced, and hand stirring resorted to. On the completion of the nitration the charges were poured into a large tank of water at a temperature of 70° F., a batch consisting of about 450 lb. After a preliminary washing in this tank the nitroglycerine was run off into a wooden swinging tub, in which it was washed five times, three times with plain water and twice with soda, a current of air working through it at the same time. The washing water was run into large tubs in which any nitroglycerine settling out from it was retained. After washing, the nitroglycerine was transferred to earthenware jars holding 60 lb. each. The jars stood for 72 hours in tanks of water warmed to 70° F., any impurities rising to the surface as scum being skimmed off. The purified nitroglycerine was poured into tin cans lined with paraffin and holding 56 lb. each, and then frozen in the tins, in which condition it was always stored and transported. This process, now 40 years old, resembles in many of its essential features, the process now in use.

With the introduction of dynamite towards the end of the Sixties, the manufacture of nitroglycerine was again taken up on a large scale, and the apparatus almost universally employed was constructed on very similar lines to that more or less in general use at the present day. The nitrating vessel was a large cylindrical lead tank with an outer wood casing, between it and the lead tank cold water circulated and it contained lead coils through which cold water ran. Agitation was effected by means of compressed air, led in through lead pipes, and in the earlier plant mechanical agitation was also employed. Glycerine was run in from a tank placed above the nitrating vessel, the inflow being controlled by means of a cock. A glass pipe led away from the cover for carrying off and observing the fumes, and the temperature during nitration was watched by the aid of a thermometer passing into the liquid through a hole in the cover of the nitrator. Below the nitrator, a large tank containing water was provided, into which the charge could be run in the event of overheating. In this apparatus several hundred pounds of glycerine were nitrated in one operation. On completion of nitration, the whole of the charge of waste acids and nitroglycerine was run slowly into a large tank of water, agitation being kept up in the tank with wooden paddles, operated by hand or mechanically. The nitroglycerine finally was allowed to separate out to the bottom of the tank, and was drawn off into smaller vats and washed several times with soda solution and water until perfectly neutral. This system entailed the loss of all the waste acids, if the inflow of the charge was not carefully controlled, dangerous heating was liable to occur, and in any case there was a large development of nitrous fumes. For these reasons this system was abandoned, towards the end of the Seventies, and the separating tank introduced. This tank is of lead and usually completely enclosed; it will be described in more detail later. The charge was run into it through a cock at the bottom of the nitrator, and nitroglycerine being lighter than the waste acid it separated out on the top of it and was then transferred to the washing tank where it was washed, as already described. When all the nitroglycerine had been drawn off, the waste acids were run away to lead tanks in another house.

The above descriptions are necessarily brief, but time does not permit of our entering into full details, or of describing the somewhat numerous differences in apparatus and processes of manufacture, which existed in the early days of the production of nitroglycerine. These are dealt with fully in "The Manufacture of Explosives" by Mr. O. Guttmann.

The relative proportions and strengths of nitric and sulphuric acids, and the proportion of mixed acid to the glycerine, have varied from time to time, and in different factories. Sobrero in his laboratory used two volumes of sulphuric acid of 1·842 sp. gr. to one volume of nitric acid of 1·424 sp. gr., and to this mixture he added half a volume of glycerine. This proportion of acids was employed in the early days of large scale manufacture, and the proportion of glycerine to mixed acid varied from one-sixth to one-eighth. The more modern practice is to use a mixture of 3 parts by weight of nitric acid of 1·5 sp. gr. and 5 parts of sulphuric acid of 1·842 sp. gr., and to nitrate one part by weight of glycerine in every 8 parts of this mixture; the proportion of glycerine to mixed acid varies somewhat according to the strength of the acids.

Theoretically, 100 parts of glycerine should produce 246·74 parts of nitroglycerine, but for several reasons this yield is never reached in practical manufacture. In the early processes a yield of somewhat under 200 per cent. was all that was obtained. In more modern factories yields between 200 per cent. and 210 per cent. were obtained, the higher figure being considered very good. The average yield at the Royal Gunpowder Factory over a series of eight years was 214¼ per cent. With the introduction of the improved plant, to be described later, a material increase of yield was obtained, the average for two years being 220·18 per cent.

With nitrating acid of the composition given above, and with commercially pure glycerine the reaction of nitration is practically quantitative. It is free from side reactions such as the oxidation of the glycerine radical, referred to in the opening sentences of Sobrero's original paper, as occurring under certain conditions. If we assume for the moment that there is no mechanical loss and that the waste acid does not contain any nitroglycerine, the operation may be stated in the form of an equation thus:—

Nitrating Acid.

$$\underset{100}{C_3H_5(OH)_3} + \left\{\begin{array}{lr} H_2SO_4 & 480.0 \\ HNO_3 & 273.0 \\ H_2O & 47.0 \\ \hline & 800.0 \end{array}\right\} =$$

Waste Acid.

$$\underset{246.7}{C_3H_5(NO_3)_3} + \left\{\begin{array}{lr} H_2SO_4 & 480.0 \\ HNO_3 & 67.6 \\ H_2O & 105.7 \\ \hline & 653.3 \end{array}\right\}$$

There are thus present in the nitrating acid 47 parts of water which appear again in the waste acid and perform no useful function. It occurred to us that, as Nordhausen sulphuric acid can now be readily obtained at reasonable prices, it might be used to remove this water. We therefore calculated this 47 parts of water to its equivalent in waste acid, and deducted the figures thus obtained from both sides of the equation. As a result, we arrived at an equation giving the composition of a nitrating acid free from water and its ratio to glycerine required to produce a waste acid of the same composition as above. This equation is:—

Nitrating Acid.

$$\underset{100}{C_3H_5(OH)_3} + \left\{\begin{array}{lr} H_2SO_4 & 266.6 \\ HNO_3 & 242.9 \\ \hline & 509.5 \end{array}\right\} =$$

Waste Acid.

$$\underset{246.7}{C_3H_5(NO_3)_3} + \left\{\begin{array}{lr} H_2SO_4 & 266.6 \\ HNO_3 & 37.5 \\ H_2O & 58.7 \\ \hline & 362.8 \end{array}\right\}$$

By using a nitrating acid free from water, it is therefore possible to reduce the quantity of waste acid produced per 100 parts of glycerine from 653·3 to 362·8, a saving of 290·5 parts. Experiments have shown, and it has been confirmed by observations on the manufacturing scale, that waste acid of the above composition absorbs 3·7 per cent. of its weight of nitroglycerine. There should therefore be obtained an increase of 10·75 per cent. in the yield of nitroglycerine if this mixed acid were adopted.

Neither theoretical considerations nor the result of experiment suggests that this anhydrous mixture would be in any way more dangerous to use than acid containing four or five per cent. of water, but in all manufactures, and in the manufacture of explosives particularly, any alteration in a process should be carried out with the utmost caution and, where possible, gradually. We did not therefore proceed at once to the use of acid free from water, but used such a strength of Nordhausen acid as would reduce the ratio of acid to glycerine from 8 to 1, to 6·13 to 1.

The manufacturing results obtained during a period of nearly two years show the increased yield that we anticipated, *viz.*, from 220 per cent. to rather over 229 per cent., and therefore prove the above reasoning sound.

In addition to the obvious economy of an increased yield, the new mixture has further advantages, inasmuch as the capacity of any given plant is greatly increased, and there is less loss of nitric and sulphuric acids through the reduction in the quantity of waste acid to be denitrated and recovered.

Having succeeded in reducing the quantity of nitroglycerine absorbed by the waste acid by adjusting the composition of the charge so that less waste acid was produced, we turned our attention to the composition of the waste acid itself. We were not aware that any thorough investigation of the absorptive properties of this acid had been published, and thought it possible that such an investigation might afford useful information.

Our earliest experiments on this point gave quite unexpected results. We were aware of the fact that the addition of water to waste acid of the usual composition caused the absorption of any globules of nitroglycerine that might be present, but we were surprised to find that if nitrating acid containing sulphuric and nitric acids in the old 5 : 3 proportion and no free water, were used, this absorption no longer took place. On the contrary, on adding a small quantity of water to the waste acid from this nitration, a further formation and separation of nitroglycerine occurred. Obviously, therefore, beyond a certain point, the less water a waste acid contains, the more nitroglycerine will it absorb.

In order to determine the nature of the curve representing the absorption of nitroglycerine in waste acid, we decided to prepare synthetical mixtures of varying composition and determine their absorptive powers. The acid mixtures to be tested were made up as follows:—Pure sulphuric and nitric acids were prepared containing exactly 100 per cent. of H_2SO_4 and HNO_3 respectively. The required proportions of these acids and of water were accurately weighed and mixed under conditions precluding any loss of nitric acid or the formation of nitrous acid. This procedure was found to be more reliable than adjustment by analysis. The method of determining the absorptive power of an acid was as follows:—100 c.c. of the acid mixture to be tested was introduced into a flask of 200 c.c. capacity, having a long narrow neck, and provided with a tubulure and stopcock at the bottom. A known weight of nitroglycerine was then added—usually about one grm. more than it was expected would be required to saturate the acid. The flask was placed in a thermostat fixed on a rocking apparatus, so that the contents of the flask could be well shaken while being maintained at any desired temperature. When saturation was considered to be complete, agitation was stopped, and the flask allowed to remain at rest in the thermostat until all the nitroglycerine had risen to the surface, leaving the acid below perfectly clear. The flask was removed and placed for a few moments in water at 19° C. If saturation were complete, a slight opalescence at once formed, but disappeared on again raising the temperature to 20° C. The clear acid layer was now run off by means of the stopcock at the bottom of the flask, the nitroglycerine being left behind in contact with only a few tenths of a gram of acid. 50 c.c. of cold water was quickly added to the flask with shaking. The dissolved acid was neutralised by addition of sodium carbonate solution and the nitroglycerine dissolved out by shaking with ether. The ethereal solution was afterwards washed, dried and distilled, and the remaining nitroglycerine weighed after desiccation. To ascertain if the nitroglycerine recovered in this way had undergone any change by agitation with the acid, its nitrogen content was frequently determined, but was not found to be altered. That concordant and reliable results can be obtained by this method will be seen from the following experiments on the time of agitation necessary for complete saturation :—

Time of agitation.	Nitroglycerine absorbed.
Hours.	Per cent.
5	3·23
8	3·25
15	3·22

While discussing the question of the absorption of nitroglycerine by synthetical waste acid, it is convenient to consider also the condition in which the absorbed nitroglycerine exists in the acid. When nitroglycerine is shaken with a mixture of sulphuric acid, nitric acid, and water, at least two phenomena are brought into play before equilibrium is established. Nitroglycerine at first dissolves in the acid without chemical change, but as soon as solution has begun, a secondary reaction sets in, which results in the decomposition of a portion of the dissolved nitroglycerine. This secondary decomposition is, we consider, due to an interaction between sulphuric acid and nitroglycerine, and results in the formation of sulphoglycerine and nitric acid. A further examination of this decomposition reveals the fact that it is incomplete even in presence of a large excess of sulphuric acid. When the solution has been allowed to stand until no further change takes place, that is, until equilibrium has been established, nitroglycerine, sulphuric acid, sulphoglycerine and nitric acid still exist in it. We have here, therefore, a case of a balanced or reversible reaction. Assuming trisulphoglycerine to be the only ester formed, the reaction may be expressed thus :—

$$C_3H_5(ONO_2)_3 + 3H_2SO_4C_3H_5 \rightleftharpoons (SO_4H)_3 + 3HNO_3,$$

but it is in reality of a much more complex nature, owing to the formation of a lower nitroglycerine, sulphoglycerine, and possibly of mixed esters.

In order to make quite certain that this interpretation of the observed facts was the correct one, we carried the investigation somewhat further. According to the now well established theory of reversible reactions, the addition to the system of excess of one of the active substances causes a displacement of the equilibrium away from the side of the equation on which that substance appears. Consequently, if this is a reversible reaction, the addition of sulphuric acid to a solution in a state of equilibrium should cause a further formation of sulphoglycerine and nitric acid, while the addition of nitric acid should conversely cause re-nitration and the formation of sulphuric acid. Both of these experiments were tried, and the displacement of the equilibrium in the direction required by theory was found to occur. Without quoting unnecessary figures on this point, it will be sufficient for our present purpose to refer to Diagrams Nos. 1 and 2. From the curves representing the ratio existing between dissolved and decomposed nitroglycerine, it will be seen that the presence of increasing quantities of sulphuric acid tends to increase the proportion of nitroglycerine decomposed ; that is to say it causes the formation of sulphoglycerine. Whereas an increase in the nitric acid content of the acid causes renitration or formation of nitroglycerine. In Diagram 3, the similar curves indicate the influence of equal increase of concentration of the nitric and sulphuric acids on the reaction. It will be seen that in this series, the influence of the latter increases at a greater rate than that of the former. Further, if this is a case of homogeneous equilibrium, from whichever side of the equation the reaction be started, the final state will be the same. Again, we find that the reaction in question proceeds according to the requirements of theory. Two experiments may be cited :—

(*a*) 3·8 per cent. of nitroglycerine was added to an acid mixture of similar composition to waste acid.

(*b*) Glycerine equal to the above 3·8 per cent. of nitroglycerine was dissolved in sulphuric acid and added to an acid mixture of such proportions that the masses of the reacting radicles present were the same as at (a) although differently combined.

Both mixtures were maintained at a temperature of 15° C., until equilibrium was established, and the quantity of nitroglycerine existing in solution determined with he following results :—

	(*a*)	(*b*)
	Per cent.	Per cent.
Nitroglycerine in solution	1·90	1·87
Decomposed nitroglycerine (by difference)	1·90	1·93

From the above evidence it is clear that the decomposition of nitroglycerine which occurs in waste acids is a reversible reaction and follows, in all respects, the laws governing such changes.

The method adopted for the determination of the ratio of what we may call potential nitroglycerine, to nitroglycerine existing as such in solution in an acid, depends on the fact that chloroform readily removes the latter without directly affecting the former and without being itself attacked by the acids. The removal of the dissolved nitroglycerine by the chloroform however, necessarily affects the equilibrium above referred to, with the result that re-nitration sets in and proceeds until a fresh equilibrium is established. For this reason it is necessary to use a relatively large volume of chloroform and to carry out the extraction in the most expeditious manner possible. Even with these precautions, however, the results obtained are not accurate. There is, however, a balancing of errors, as on the one hand nitroglycerine is formed during the period of extraction however short—the velocity of reaction of re-nitration being greatest during its first period ; on the other hand, one extraction, even with a large volume of solvent, will not remove the whole of the nitroglycerine in solution. The results obtained by this method are, therefore, probably fairly accurate.

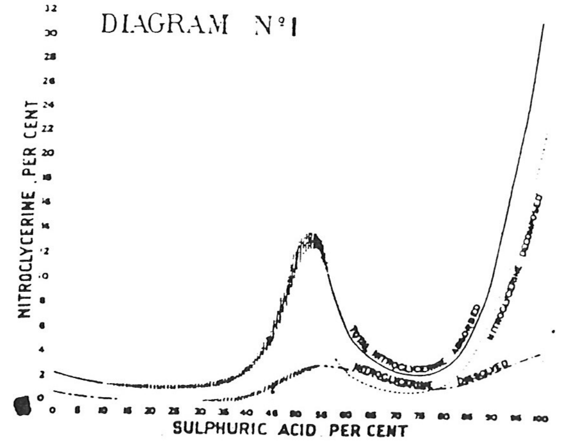
Waste acid contains three principal ingredients, sulphuric acid, nitric acid and water. Three series of experiments were therefore designed to show in what manner and to what extent each ingredient influenced the proportion of nitroglycerine required to saturate the acid. Thus :—

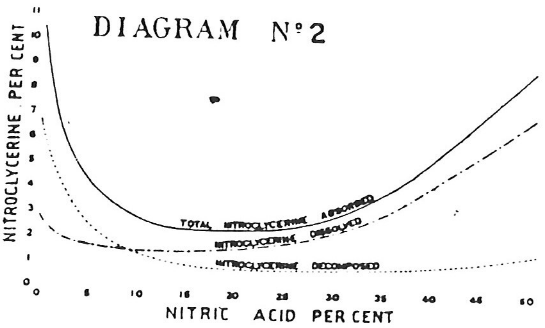
Series I Ratio $\frac{H_2O}{HNO_3}$ = a constant (1·1) ; sulphuric acid the variant.

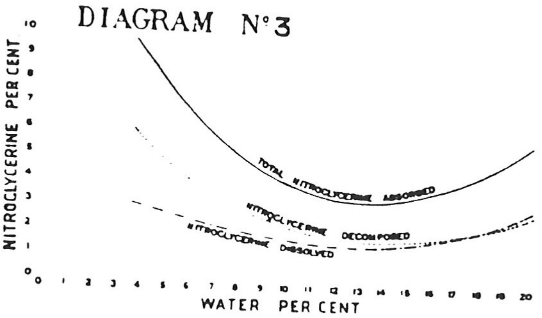
Series II Ratio $\frac{H_2SO_4}{H_2O}$ = a constant (5·8); nitric acid the variant.

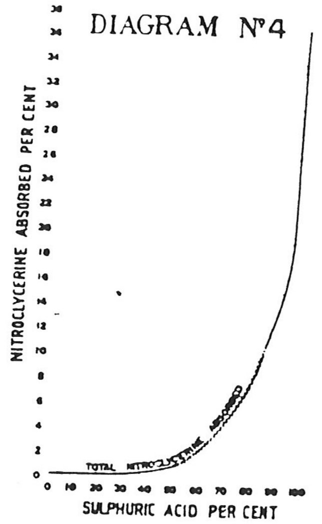
Series III Ratio $\frac{H_2SO_4}{HNO_3}$ = a constant (10·4) ; water the variant.

The results of these three series of experiments are given in Diagrams 1, 2 and 3. It will be seen that in the experiments where sulphuric acid was the variant, a portion of the curves are represented in shaded lines. This indicates that, on attempting to saturate acids in this zone, oxidation of the glycerine radicle occurred and the results were vitiated. In these cases special precautions were taken, and the reaction was never uncontrollable, but it is clear that no acid of a composition in or near this zone should be allowed to come in contact with nitroglycerine in a manufacturing operation. In this connection, the action of sulphuric acid of various strengths on nitroglycerine was examined, with the results shown on Diagram 4. Again, it will be seen that a danger zone exists, namely, with sulphuric acid containing between 50 and 85 per cent. of H_2SO_4. As regards nitric acid of various strengths, up to 45 per cent. HNO_3 no action was found, but above this oxidation occurred. The upper limit of this zone









of decomposition is below 90 per cent. of HNO_3, but it was not considered necessary to investigate this point too closely, owing to the danger of turbulent or even explosive reaction. It was, however, proved that nitroglycerine is miscible in all proportions with nitric acid containing 100 per cent. HNO_3, and such a solution containing 10 per cent. of nitroglycerine can be raised to a high temperature without decomposition taking place.

Returning to Diagrams 1, 2, and 3, it will be seen that in the case of each variant there occurs a point of minimum absorption of nitroglycerine, and in all three cases this minimum is lower than the absorption shown by ordinary waste acid. It was therefore probable that the present composition of waste acid could be improved on and we were confronted with the problem of how to select from an infinite number of possible mixtures, the one which would be the most economical from the manufacturers' point of view. The time at our disposal this evening does not permit us to give an account of the results so far obtained. The investigation of this point has proved long and intricate, and is, even now, incomplete as regards some of the factors of minor importance.

Mixed acid.—Having determined on theoretical grounds an acid mixture of suitable composition, which, whilst producing a waste acid of the usual strength, would at the same time allow of a much smaller proportion of acid to glycerine being employed than heretofore, we decided to use for the production of this mixture a Nordhausen acid offering no difficulties in use. An acid containing 20 per cent. of SO_3 is liquid at all ordinary temperatures. Supplies of this acid were accordingly obtained, and it has given no trouble of any kind. The acid is supplied to the factory in iron drums, containing about half a ton each; the drums are stored in the open, and are emptied into a steel egg of about 3,000 lb. capacity, and the acid blown from it into the mixing tanks. The mixing tanks are large, cylindrical, steel plate tanks, raised a few feet from the ground. The tanks, of which two are in use, have a capacity of about 60 tons of mixed acid. In the cover is an inlet cock for the sulphuric acid, and a lead inlet pipe extending to the bottom of the tank, for the admission of nitric acid. Two lead pipes also pass through the cover down to and along the bottom of the tank, for supplying compressed air. The nitric acid made by the Valentiner process, which produces an acid very free from nitrous acid, is first of all run into the tank. The sulphuric acid is then blown in slowly from the egg. During the time that the sulphuric acid is being added, air agitation is maintained in the tank. An earthenware fume pipe leads from the cover of the tank to a battery of Guttmann ball towers, so that the fumes arising from the mixing are condensed. By using such large tanks a more uniform acid mixture is obtained, and with two tanks it is possible, whilst acid from one is being used, to fill the other some days before it is required; this allows any solid impurities to settle out, with the result that a very clear nitrating acid is obtained. This is a point of much importance, as our experience has proved that the time required for the nitroglycerine to separate from the waste acid is influenced by the clearness of the nitrating acid. A dirty nitrating acid very much prolongs the separation of the nitroglycerine. Another advantage of these large mixings, prepared some time before they are required for use, is that they can be analysed, and should the mixture not be correct, it can be accurately adjusted by the addition of either sulphuric or nitric acid, as may be required. The mixed acid when required for use is drawn off into a steel tank, and blown into a cylindrical steel vessel in the charge house, at a higher level than the apparatus in the nitrating house. This steel vessel resembles a vertical egg in construction. The top is provided with a small aluminium dome with a fume pipe leading up through the roof, so that there are no fumes escaping into the charge house. The acid supply pipe is led in through the aluminium dome, and terminates in a swan neck, the open end of which coincides with the level of the charge required. A gauge glass is fixed to the aluminium hood. The gauge is watched whilst the acid is flowing in, and when the acid level in the gauge glass is slightly above the charge level, the air pressure on the mixing tank egg is released. The supply pipe acts as a syphon, drawing off any surplus acid, and thus automatically adjusting the volume of the charge. This arrangement ensures an absolutely correct charge of nitrating acid without any of the trouble, inconvenience, and possibility of errors of weighing.

Glycerine.—Glycerine from various sources of supply is used, and to ensure uniformity throughout manufacture, the different glycerines in stock at any one time are blended proportionately to the stock quantities. The blending takes place in iron tanks of a capacity of about 10 tons. One blend of glycerine corresponds to one mixing of nitrating acid. The glycerine is rendered sufficiently fluid by heating, to enable it to be blown from a steel egg into a galvanised iron tank in the charge house. This tank is provided with coils permitting of the glycerine being either cooled or heated, as required. The glycerine is run from this tank into the glycerine tank in the nitrating house; this latter tank is provided

DIAGRAM NO 5

R.C.P.F. NITRATING HOUSE PLANT.

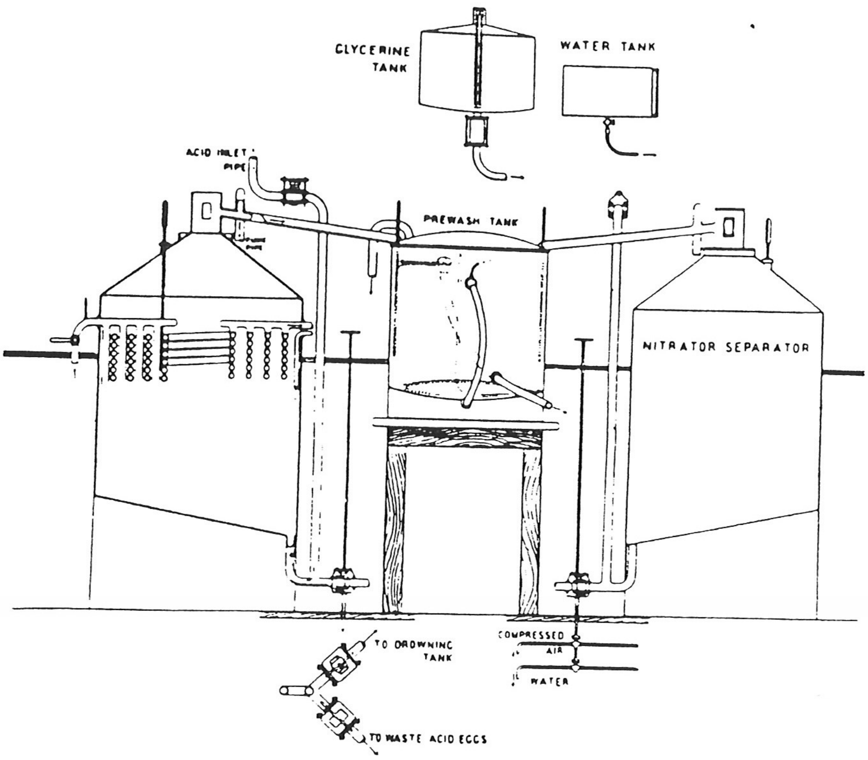
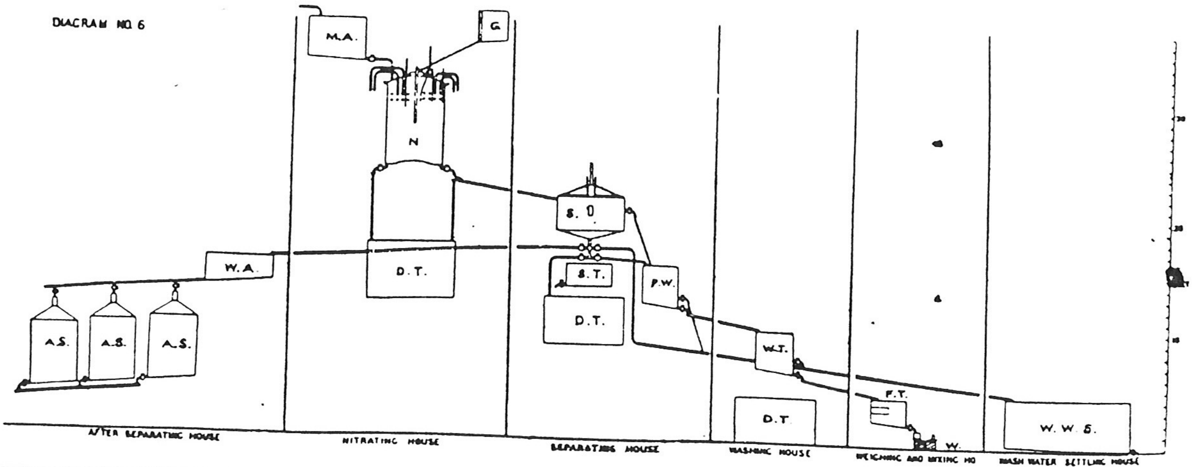
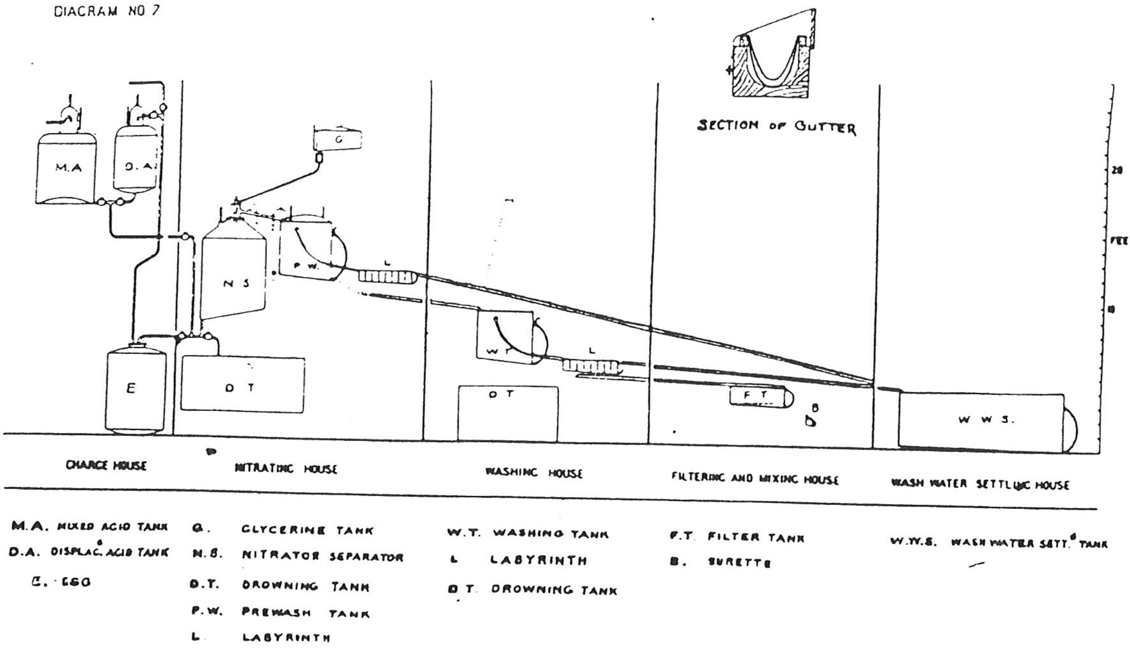


DIAGRAM NO 6



W. A	WASTE ACID TANK.
A S	AFTER SEPARATING BOTTLES
M.A	MIXED ACID TANK
G.	GLYCERINE TANK
N.	NITRATOR
D.T.	DROWNING TANK
S.	SEPARATOR
S.T	SAFETY TANK
D.T.	DROWNING TANK
P.W.	PREWASH TANK
W.T.	WASHING TANK
D.T.	DROWNING TANK
F. T.	FILTER TANK.
W.W.S.	WASH WATER SETT^G TANK
W	SCALES.

DIAGRAM NO 7



with a gauge glass so arranged as to allow of accurate measurements of the charge. In the case of the glycerine, as in the case of the acid, and for the same reasons, the charge is measured, not weighed.

Nitration.—We have already referred to the nitrating plant used by Nobel for the production of nitroglycerine on the large scale, for the manufacture of dynamite, when the latter explosive was introduced. This plant, with but few modifications, was universally used until recently for the production of nitroglycerine. We propose to describe this plant, as erected at the Royal Gunpowder Factory, in 1890, and to compare it against the plant now in use there, as well as at other factories in this country and abroad. These plants are shown on diagrams Nos. 6 and 7.

The old pattern nitrating apparatus was a large lead tank, cylindrical in shape with a convex bottom; inside were coils, through which cold water circulated and pipes for the supply of compressed air were led down to and round the bottom of the apparatus. The top of the tank was closed by a dome cover of lead, cemented on, and provided with glass inspection windows. The air pipes, the pipe conveying the acid, and the water inlet and outlet pipes, all passed through holes in the cover; in the centre of the cover was a manlid with an acid lute, and in the centre of that again was a hole for the insertion of the glycerine injector. This hole was closed by a loose lead plug when the injector was removed. A fume pipe fitted with a glass cylinder, to allow the colour of the fumes to be seen, was also fixed in the cover. The bottom of the tank was provided with two earthenware cocks. Both cocks were available for drowning the charge; whilst one of them was used for running the contents of the nitrator into the separating tank through a movable lead bend.

The nitrating acid having been run into the nitrator, the glycerine injector was introduced through the hole in the manlid, and the glycerine sprayed by means of air pressure under the surface of the acid. During nitration cold water was allowed to circulate through the coils, and the contents of the nitrator were kept agitated by means of compressed air. The inflow of glycerine was regulated so as to keep the temperature of the charge at or below 22° C. When all the glycerine had been added, the injector was removed, the charge cooled down to about 15° C., and then run off into the separator.

Separation.—The separator was a square lead tank; the bottom sloped downwards from all four sides to a central hole fitted with a vertical glass cylinder. A horizontal pipe with branches in four directions was secured to this cylinder, each branch was provided with an earthenware cock. Under the separator was a lead-lined wooden tank, for the purpose of catching the contents of the separator, should the glass cylinder break from any cause. The separator was provided with a skeleton frame cover, filled in with glass, the sides sloping up to a fume pipe, for carrying off the fumes; air pipes were led into the separator through the cover. On one side of the separator was a glass inspection window, on another side was an earthenware cock, situated about 4″ below the surface of the nitroglycerine, when it had separated from the acid. When the separation was complete, the bulk of the nitroglycerine was run off through the earthenware cock in the side of the separator into the preliminary washing tank. The waste acid was then run away through one of the branches on the bottom pipe, to the "after-separating house." As soon as the rest of the nitroglycerine was seen coming down into the glass cylinder, the earthenware cock leading to the after-separating house was closed, and the one leading to the pre-wash tank was opened, and the remainder of the nitroglycerine run into this tank. Of the other two cocks at the bottom of the separator, one was used for running any thick sludge to the "wash-water settling house," the other was connected to the "drowning tank."

In some factories, instead of a closed separator, an open lead-lined tank was, and is still, used. The nitroglycerine, as it separates from the waste acid, is removed from the tank by hand, by means of a metal skimmer, and transferred little by little to the preliminary washing tank.

In the apparatus just described, it will be noticed that there are several earthenware cocks, in fact, earthenware cocks were until comparatively recently a feature of all the plant employed in the manufacture of nitroglycerine. These cocks have always been regarded as a source of danger, owing to the possibility of friction being set up between the body of the cock and the key, when the latter was manipulated, should any foreign gritty substance be present. Where nitroglycerine only had to be run out of a vessel, it had been found possible to do away with the use of earthenware cocks, in a manner which will be referred to presently, but the same system could not be applied where acids or acid nitroglycerine had to be dealt with. We had at the Royal Gunpowder Factory done away with the use of earthenware cocks in all the plant subsequent to the separator, but they existed as late as 1901 in the nitrating apparatus, and in the separator. In January of that year, the danger incidental to the use of earthenware cocks was brought home to us in a forcible manner. Shortly after the charge had been run out of the nitrating apparatus, an explosion occurred in one of the earthenware cocks leading to the drowning tank. The cock was not being used at the moment the explosion occurred, and the explosion was therefore probably due to the lodgement in a depression of the key, of a trace of acid nitroglycerine. If the apparatus had contained the charge, a serious accident must inevitably have occurred. This accident emphasised the necessity of doing away with the earthenware cocks still remaining in our plant, through which nitroglycerine passed, and the idea occurred to us that this would be accomplished if we could remove the nitroglycerine, which on the completion of nitration separates out on the surface of the acid. from the top of the apparatus, instead of from the bottom. The simplest way to effect this was, if possible, to raise the whole of the contents of the apparatus, so that the nitroglycerine should flow over a suitable arrangement in the cover, and run by gravity into the pre-wash tank. The best method for raising the level of the separated nitroglycerine was to introduce some inert liquid below the nitroglycerine, and the liquid obviously most suitable for the purpose was waste acid from a previous charge. Waste acid was the liquid we selected, and the form of apparatus eventually adopted to carry out this principle is shown in diagram 5. The construction and method of working this apparatus we will now describe.

The "nitrator-separator," as we prefer to call it, consists of a cylindrical lead vessel with a bottom sloping in one direction, and containing cooling coils and air pipes, the number depending upon the size of the vessel. The cooling coils enter and leave the vessel through its sides, just below the surface of the nitrating acid, as do also the air pipes. The cooling water is led in and led out again through one main pipe controlled by a single cock, the coils themselves branch away from this main pipe inside the vessel. The supports for the coils are of lead and are formed by loading up between the turns; this arrangement obviates the use of lead covered iron supports, and entirely does away with interstices in which nitroglycerine or sulphate can lodge. The cover is conical, and is burnt on to the cylindrical portion. The cover terminates in a cylinder of small diameter open at the top and provided with glass inspection windows; the only other fitting in the cover is a gland through which the thermometer passes. A pipe is fixed in one side of the cylinder, from which another pipe branches, for carrying away the fumes. A suction is produced in this pipe by means of an air jet. Beyond this fume pipe, the pipe from the cylinder opens out into a gutter leading into the pre-wash tank. The pipe for conveying the nitrating acid as well as the waste acid for displacement, enters the apparatus at the bottom. The pipe is carried vertically downwards below the level of the bottom of the apparatus, and then rises again into it; the object of this arrangement is to prevent the possibility of nitroglycerine getting into the acid supply pipe. There are two branches on this pipe, each with an earthenware cock; one branch leads into the drowning tank, the other to the waste acid egg. The drowning cock is controlled by means of a long rod terminating in a handle, situated on the operating platform. By turning this handle through a quarter of a circle, the drowning cock is opened, and allows the whole of the contents of the nitrator-separator to discharge into the drowning tank. Attached to the key of the drowning cock are two other cocks, one on the drowning tank compressed air pipe, the other on the water supply pipe, so that by turning the handle, not only is the drowning cock opened, but the drowning tank compressed air supply is turned on, and water is also admitted to the drowning tank. The drowning tank is always kept full of water, and is provided with an overflow, so that the water is being continually renewed during the drowning of the charge. This drowning arrangement has the advantage of simplicity, and the continual supply of cold water keeps down the temperature due to the mixing of a large volume of acid with the water, and also allows of a smaller drowning tank for any given charge.

The waste acid from the previous charge having been run out of the vessel, the cock on the nitrating acid tank is opened, and the acid allowed to run into the nitrator-separator by opening the cock on the acid supply pipe. As soon as the acid has all run in, the cock on the nitrating acid tank is closed, as well as the cock on the acid supply pipe. The nitrating acid having been brought to the desired temperature by means of the cooling coils, the injector is inserted through the open top of the apparatus, and the nitration commenced. The temperature of the cooling water which flows through the coils, is regulated so that the total time of nitration for any given charge is kept constant within fairly narrow limits, both summer and winter. To enable this to be done the water is refrigerated when necessary. The advantages of using refrigerated water are, that nitration is completed in a reasonable time, loss of nitric acid due to volatilisation is reduced to a minimum, and the time of nitration being constant, enables the whole of the operations in the factory to be carried out systematically. The volatilised nitric acid is carried away to a Guttmann condensing tower, provided with a liquid circulating arrangement; this allows of a complete condensation of the fumes, and the recovery of about 18 lb. of nitric acid of a sp. gr. of 1·320 per ton of nitroglycerine produced. When nitration is completed the injector is removed and the nitroglycerine allowed to separate for a few minutes. The cock leading from the displacement waste acid tank is then opened, and waste acid is allowed to enter the apparatus at the bottom, by opening the cock in the acid supply pipe. The rate of inflow of displacing acid can be regulated with the utmost nicety, so as to allow of the nitroglycerine as it separates flowing over through the gutter into the pre-wash tank. The dividing line between the clear nitroglycerine and the acid is watched through the inspection windows.

GUTT
MANN

The advantages of separating the nitroglycerine in the nitrator-separator are, that the nitroglycerine is removed from the acid as quickly as it separates, the cooling coils, which did not exist in the old form of separator, are a great safeguard against any undue rise in temperature, which could only be dealt with formerly by drowning the charge; and any flocculent matter separating from the charge is distributed throughout the whole bulk of the nitroglycerine, instead of accumulating, as formerly, as a thick sludge between the nitroglycerine and the waste acid. When the separation is complete, a clear line of demarkation between the nitroglycerine and the waste acid appears in the inspection windows.

The nitrator-separator is left full of waste acid until it is required for the nitration of another charge. The result of this is that no part of the interior of the apparatus is exposed to acid fumes, and its durability is increased to a very remarkable extent. In the old form of apparatus, where this could not be done, and where the coils entered through the cover, it was necessary to remove the cover and the coils as often as once in every three months, to repair them. The new pattern apparatus was in use for 2¼ years without being opened up. After that period it was considered desirable to remove the cover for inspection. The whole of the interior of the apparatus, as well as the cooling coils and the air pipes, were found to be as good as new, and no repairs of any kind were necessary. As a precaution, the cooling coils are tested every week, before commencing work, by air pressure; any leak would be at once detected by the escape of air through the waste acid.

Preliminary washing.—The old pattern of pre-wash tank was fitted with two earthenware cocks, the upper one for running off the washing waters, the lower one for running off the nitroglycerine to the washing house. The air pipe for agitating the charge during pre-washing operations was laid loosely on the bottom; another was led into the bottom faucit down the inside of the tank; the tank was open at the top.

The pre-wash tank now in use has no cocks. It has a fixed lead cover with an opening covered with a small rubber flap. There is a fume pipe in the cover, for removing the fumes. The washing waters are run off through a skimmer of pure rubber, in the form of a tube, the top expands into a funnel provided with a loop handle, also of rubber. By means of this handle, the operator depresses the skimmer gradually, and allows the wash-water, as it separates, to flow over the edge of the funnel and away down the tube. The skimmer delivers into a labyrinth where the bulk of the nitroglycerine contained in the wash water separates out. This nitroglycerine is drawn off into a rubber bucket, and returned to the pre-wash tank. The bottom faucit has secured to it a rubber tube. During the pre-washing this tube is in position on a perforated plug, into which compressed air is led; this ensures the nitroglycerine in the rubber tube being pre-washed along with the rest of the charge. The air pipe in the pre-wash tank, instead of being laid loose inside, is burnt on to the under-side of the bottom. The air holes are pierced through the bottom, and are bushed with ebonite plugs, to prevent wear. The advantages of this form of air pipe are, that it entirely removes the risk of any friction between the air pipe and the bottom of the tank which might be set up by vibration due to escaping air when the pipe is loose, it gives a perfectly flat surface on which no sulphate or other solid impurities can lodge, and it facilitates the cleaning out the tank between the charges. The pre-washing is cted by means of water, soda solution being used for the last pre-washing to render the nitroglycerine alkaline before it is run down into the washing house. When the charge is ready for sending down to the washing house, the end of the rubber running off pipe is slipped off its plug and placed on a fixed nozzle on the end of the gutter leading to the washing house. No clamp of any sort is used on this pipe, either to cut off or to regulate the outflow of nitroglycerine; hand pressure is sufficient for both these purposes. The gutter connecting the pre-wash tank to the washing house tank, passes through the open, and to prevent freezing of the nitroglycerine during the cold weather, it is provided with an outer jacket. (See Diagram 7.) Warm water is circulated between the gutter and the jacket when the external temperature renders this necessary. In order to have a gutter with a perfectly smooth even surface, the old system of lap-jointing has been replaced by a butt jointed gutter, scraped smooth on the inside. This pattern of gutter has been in use for years, and has shown no signs of developing cracks or unevenness, which were of not unfrequent occurrence in the case of lap-jointed gutters. The gutter instead of being covered with V-shaped heavy wooden covers, is protected by means of a canvas covering fixed along one edge and laced down on the other, so as to enable it to turn back readily for cleaning purposes. After a charge has been run down, the gutter is wiped along its whole length with a flannel in the direction e washing house, to remove all traces of nitroglycerine.

ashing.—The old washing tank was usually a wooden tank lined with lead and provided with cocks, one at the bottom for running off the nitroglycerine, and one or more skimming cocks at different levels. An alternative arrangement for running off the wash-water was a skimmer, a saucer-shaped vessel attached to a rubber pipe, which led out through the side of the tank to the wash-water gutter. The early form of skimmer was of lead and was supported by means of a rope and counter weight. Later patterns were made of lighter material, for example, sheet brass covered with rubber cloth. The use of the skimmer got rid of the earthenware cocks for running off the wash-water, but the objectionable bottom cock for running off the nitroglycerine remained. The pattern of tank now in use at the Royal Gunpowder Factory is made of heavy lead without any wood casing. It has no cocks. The air pipe is an underneath one on the same lines as the one in the pre-wash tank, but the wear of the air holes is so slight that it has not been found necessary to bush them with ebonite. The skimmer has no saucer-shaped top to it, it is entirely of rubber and exactly similar to the one in use at the pre-wash tank. The nitroglycerine is run off through a rubber tube in the same way as it is run off from the pre-wash tank. The wash-waters are run through a labyrinth. The nitroglycerine is carried by a water-jackotted gutter to the filtering and mixing house. The drowning arrangements are on the same lines as those of the nitrating house. The washing tank is provided with a hood of rubber cloth with a funnel, also of rubber cloth, passing out through a hole in the roof. An air-jet is inserted in the funnel, and all fumes are removed from the house. To enable the operator to know how much washing waters to add and when they have been removed, an inch scale is marked down the inside of the tank. This arrangement obviates the use of a loose measuring rod.

Just prior to running down the charge of nitroglycerine from the pre-wash tank, some warm soda solution is sent down the gutter from the nitrating house. This is immediately followed by the charge of nitroglycerine, and the charge of nitroglycerine is itself immediately followed by some more warm soda solution. Purification of the nitroglycerine in the washing tank is effected by washing it with warm weak soda solution, agitation of the contents of the tank being kept up all the time by the means of compressed air. To remove the sodium carbonate as far as possible, the last two washings, at least, are carried out with warm water.

The water available at the Royal Gunpowder Factory is very hard, and in course of time the interior of the washing tank showed a tendency to become coated with an extremely hard deposit consisting chiefly of carbonate of lime. To prevent the formation of this very objectionable scale, the practice now is to soften the water and to filter it very carefully before use. The softening and filtering processes are applied to all washing water used in the manufacture of nitroglycerine, and the softened and filtered water, as well as the soda solution at the proper temperature, are supplied to all the houses from main supply tanks in the charge house. This arrangement does away with the making up of soda solutions and the heating of water in any of the houses themselves.

An important feature in connection with the washing operation is the design of the washing tank, as affecting the total depth of liquid it contains. The greater the depth, the longer is the time the nitroglycerine takes to separate from the washing waters. Two series of experiments on this point have been carried out at different times. The depth of liquid was varied, the proportion of nitroglycerine to washing water remaining constant. In one case the total depth of liquid was 27½ inches, in the other 18½ inches. With the greater depth of liquid the mean time of separation of the first washings of a number of charges was 34½ minutes in the first series, and 28½ in the second; with the lesser depth of liquid the mean time of separation of the first washings of a number of charges was 10 minutes in the first series, and 9½ minutes in the second.

Filtration.—The filtration of the nitroglycerine is generally carried out in the washing house in a lead lined wood tank. This tank is provided with a cover in which a cylinder, open at both ends, is placed; the bottom of the cylinder is closed by means of a wire gauze attached to a solid metal ring, and this supports a flannel bag filled with salt. The nitroglycerine runs through the salt filter into the body of the tank, moisture being absorbed by the salt and any flocculent matter being retained on the bag. The nitroglycerine is run out of the tank through an earthware cock into some suitable vessel placed on scales for weighing the charge. The cylinder, the wire gauze with ring, and the bag of salt, were all of necessity removable, and at the end of the day's work, or oftener if necessary, the salt bag had to be renewed, and the salt dissolved in warm water to recover any nitroglycerine it might contain.

The filter tank at the Royal Gunpowder Factory is a plain lead tank with a fixed false bottom of perforated lead, a layer of sponges sewn up in flannel is laid on the false bottom. The nitroglycerine is run on to the surface of the sponge bags, through which it filters. The sponges retain the moisture and any flocculent matter. As often as is necessary the sponges are removed and wrung by hand, to free them from water and any nitroglycerine. For drawing off the nitroglycerine the usual rubber tube is employed. Instead of using a movable vessel on scales, the nitroglycerine is run into a fixed burette of lead provided at the top with a very narrow orifice, to allow of accurate measurement. The requisite charge, measured in this way, is emptied out of the burette, through a rubber tube, into rubber-lined canvas bags containing the weighed charge of guncotton. It will be seen that this pattern of filter tank, burette, and rubber bag, do away with all movable apparatus, tending to very much greater safety in the manipulation of the pure nitroglycerine. The substitution of the sponge filter for the salt filter, reduces the amount of sodium in the finished explosive, which is not without its effect on the luminosity of its flame.

The charge is sampled from the filter tank. The sample is taken in small guttapercha bottles about the middle of the running off of the charge, precautions being taken to obtain an absolutely fair sample.

The heat-test is the most important test to which nitroglycerine is subjected. Experiments carried out some time ago demonstrated that the heat-test was very much influenced by the percentage of sodium carbonate retained in the finished nitroglycerine. These experiments were very instructive, and the following is a brief resumé of the results :—

	Heat test at 180° F.	
	I.	II.
	mins.	mins.
Nitroglycerine—		
From filter tank	88	70
After drying in desiccator (sodium carbonate retained)	57	66
After washing with distilled water and drying in desiccator	—	20
After thorough filtration through paper	21	18

To obtain true results, therefore, the sample should be thoroughly freed from sodium carbonate before heat-testing. Nitroglycerine is also tested for moisture, alkalinity and nitrogen content.

Wash-waters.—All the waters used for washing nitroglycerine and plant, are run down lead gutters into a large wooden tank in the wash-water settling house, the contents of the tank being kept agitated by means of compressed air. At the end of the day's work, the air is shut off, and any nitroglycerine present is allowed to settle out, and is drawn off through the usual rubber pipe into buckets and returned to the preliminary washing tank in the nitrating house. At the end of the week the mud, consisting mostly of sulphates holding a certain proportion of nitroglycerine, is removed from the wash-water settling tank to flannel filters suspended over a small lead washing tank. The nitroglycerine is washed out of the mud by means of hot water and soda solution. This treatment has the advantages of removing nitroglycerine, rendering the mud alkaline and converting the sulphates originally present into carbonates; the mud in this condition is much less likely to decompose. Analyses have shown as much as 80 per cent. of lead sulphate in the mud as removed from the wash-water settling tank, practically the whole of which is converted into lead carbonate by the alkaline treatment. The mud is subsequently wrung in flannel to remove the last traces of nitroglycerine and then mixed with paraffin and burnt.

Since the adoption of labyrinths in the nitrating and washing houses for passing the wash-water through, the quantity of nitroglycerine which finds its way down to the wash-water settling tank has been very materially reduced. Formerly, the quantity of nitroglycerine recovered from the wash-water settling tank amounted to about 4½ per cent. of the nitroglycerine manufactured. The percentage now is about 1½. The better settling now given to the nitrating acid, and the use of softened water have materially reduced the amount of mud. Whereas formerly the mud amounted to about half per cent. of the nitroglycerine, it is now only one quarter per cent.

After-separation.—The after-separating house contained large lead vessels with conical tops provided with a small glass separation cylinder in the centre. The small quantities of nitroglycerine settling out from the waste acid were removed from time to time by means of a metal skimmer, and drowned in a small washing tank full of water. Apart from the fact that decompositions of the acid nitroglycerine occasionally took place, this house was an expensive one to install and maintain, and required constant supervision as long as any waste acid was present in it. The quantity of nitroglycerine that was recovered was incommensurate with the labour required and the cost of maintaining the installation.

The after-separating house has for some time ceased to exist at the Royal Gunpowder Factory. To enable us to dispense with this house, we made use of the fact that the addition of water to the waste acid not only prevented the formation of more nitroglycerine, but absorbed any nitroglycerine existing as such in a fine state of division in the waste acid. In the original experiments it was ascertained that at the normal working temperature of the factory, *viz.*, from 10° C., to 15° C., the addition of 2 per cent. of water sufficed to prevent the separation of nitroglycerine from the waste acid on storage. An accident with a drum of nitroglycerine waste acid, which occurred at an acid factory in January, 1906, led to further experiments being carried out by us on this point. Waste acids from actual nitrations were operated upon. These were kept at various temperatures for considerable periods without and with an addition of 2 per cent. and 5 per cent. of water. The results showed that when any nitroglycerine did separate from the acids, the quantity separated varied inversely with the temperature of storage, that 2 per cent. of water did not entirely prevent the separation of nitroglycerine below 10° C., and that with 5 per cent. of water no nitroglycerine separated, even when the acids were kept at a temperature of 0° C. Experiments carried out at the same time, in which nitroglycerine was actually added to waste acids containing different percentages of added water at the same, and at different, temperatures, brought out the fact that the absorptive power of the acids increased with the increasing percentages of water, and with rise of temperature. These latter experiments explained the cause of the phenomena observed in the manufacturing experiments referred to above.

The study of the influence of the addition of water to waste acid led to the method of dealing with waste acid by after-separation in a special house being abandoned in favour of a simpler and less expensive method. The waste acid is now allowed to remain in the nitrator-separator until it is required for another nitration, any nitroglycerine separating in the interval being displaced in the usual way into the pre-wash tank. This further separation of the nitroglycerine is promoted by cooling down the waste acid. When the nitrator is to be emptied, every trace of nitroglycerine is removed from the surface of the acid; the quantity of waste acid required for the displacement of a subsequent charge is then run out of the nitrator into an egg, and blown into the displacing acid tank in the charge house. To the remainder of the waste acid in the nitrator, 2 per cent. of water is added, the contents of the nitrator, meanwhile, being strongly agitated by means of compressed air. The waste acid is then sent into an egg and blown over to a tank in the denitrating house. As a further precaution against a possible separation of nitroglycerine, all waste acid is kept at a temperature of about 15° C.

The plant and the systems of manufacture we have described in detail, are shown diagrammatically on diagrams No. 6 and No. 7. Diagram No. 6 exhibits a factory typical of many in this country and abroad. Diagram No. 7 is a diagram of the nitroglycerine plant of the Royal Gunpowder Factory and of some other English and foreign works. The plants shown on the diagrams are both for the nitration of a charge of 1320 lb. of glycerine. The Royal Gunpowder Factory diagram No. 7 differs from the factory shown on diagram No. 6 in the following main points :—

1. Reduced total elevation 16 ft., against 33½ ft., measuring from the top of the nitrator to the bottom of the wash water settling tank.

2. Less total ground area. The simplest way to

estimate this is to take the number of the gutters, connecting house to house. In diagram 6 plant there are 5 such gutters, in diagram 7 plant only 3, so that the respective ground areas are as 5 to 3. For a 5,000 lb. limit of nitroglycerine the length of each connecting gutter measured from outside to outside of any two houses, must be, according to the Home Office distances, 51 yards.

3. Omission of the separating house.
4. Omission of the after-separating house.
5. Fewer pieces of apparatus. For nitrating and separating there are 5 vessels in diagram 6 plant and 2 in diagram 7 plant; for diagram 6 plant there is also the addition of the after-separating house apparatus.
6. Abolition of all cocks, except those for acid to and from the nitrator-separator.
7. Measuring acids, glycerine, and nitroglycerine, instead of weighing them.
8. Introduction of labyrinths for all washing waters.
9. Simplification of plant generally.

The Royal Gunpowder Factory plant tends to increased safety in manufacture for the following reasons:—

1. The absence of earthenware cocks removes the risks attendant on their use. These risks are, friction due to the presence of some foreign substance, jamming due to nitroglycerine freezing or through want of lubrica- , and decomposition of acid nitroglycerine lodging in them.
2. The removal of the nitroglycerine from contact with the acid as it separates out from it.
3. The presence of the cooling coils during separation in the nitrator-separator.
4. In factories where nitration and separation are carried out in separate houses, the undesirable operation of running the mixture of acids and nitroglycerine down a more or less exposed gutter is avoided.

It is important to note from the point of view of risk to personnel, that for any given output, fewer men are required for working diagram 7 plant than for working diagram 6 plant, and the whole of the former plant being enclosed and provided with arrangements for carrying off both acid and nitroglycerine fumes, the men work under much more healthy and pleasant conditions. In addition to the increased yield, amounting to at least 15 per cent., there are many other economical advantages which it is unnecessary to enumerate.

We wish in conclusion to refer to a matter we consider of paramount importance in connection with the safe manufacture of nitroglycerine, and that is the absolute necessity of entirely dispensing with the use of any heavy or hard loose tools and implements in the houses. The abolition of all such articles has been a guiding principle with us in designing and perfecting the plant which we have described, and that we have succeeded in accomplishing this will be evident from an inspection of the of tools and implements allowed in the various houses.

The lists of authorised articles are termed "Use lists," and the use lists for the various houses are as follows:—

Articles.	Nitrating house.	Washing house.	Washwater settling house.	Filtering and mixing house.
Bags, rubber	—	—	—	1
Bottles, guttapercha	—	—	—	12
Buckets, rubber...	3	6	6	—
Covers, bucket, guttapercha	—	6	6	—
Flannels..........	4	3	2	2
Gauntlets, rubber .	1	—	—	—
Gauntlets, leather	—	—	—	2
Overshoes, rubber	4	3	2	—
Socks	—	—	—	2
Thermometers	3	3	2	—

The list for any one house is posted upon a board near the entrance of that house. This board also shows the quantity of explosives and the number of men allowed in the house in accordance with the usual practice in explosives factories as required by His Majesty's Inspectors of Explosives.

Some of the more recent accidents which have occurred in nitroglycerine manufacture have been attributed to the dropping or fall, or knocking over of some heavy tool or implement, and in view of the fact that we have proved that the presence of any such articles in houses used for the manufacture of nitroglycerine is absolutely unnecessary, we venture to hope that it will not be long before His Majesty's Inspectors of Explosives will require that tools and implements likely to cause an accident shall be excluded altogether from the houses, and that "use lists" shall be affixed to every house in the same way that "limits" of explosives and men now are.

We are indebted to the Master General of the Ordnance for permission to publish this paper.

Discussion.

The **Chairman** mentioned the difficulties which in the early days attended the use of glycerin prepared from soap lyes in the manufacture of nitroglycerin. Frequently there was a separation of flocculent matter, sometimes honeycombing the whole mass of the nitroglycerin. The authors had mentioned impure acid as causing this abnormality; but in his own experiments chemically pure acid was always used. He could mention several substances which, added in minute quantities to the glycerin, would produce the separation of flocculent matter. Moreover, this flocculent matter was not only confined to soap lye glycerin. He should therefore like to ask whether the authors could throw any further light upon the cause of this separation. He noticed that they had got over the difficulty in a very ingenious manner by floating it off. Regarding the reaction of the sulpho-esters of glycerol, some light might be thrown on the equation by the fact that on trying to prepare glycerides from glycerine sulphate with fatty acids, only mono- and di-glycerides, and not tri-glycerides were obtained.

Mr. **H. F. Donaldson** referred to the great advantages which accrued from every effort to eliminate danger in hazardous operations which attached to such things as cocks in the nitroglycerin apparatus, and to the exclusion of all but absolutely necessary movable appliances in houses devoted to this manufacture. The paper contained valuable information on the chemical side of the question, as it certainly did on the safety of *personnel*.

Lt.-Col. Sir **Hilaro Barlow** said the point of greatest interest to him in connection with any paper on explosives was that of safety. All who had to do with the British workman would know the extraordinary importance of making, if possible, every safety appliance in a factory automatic; *e.g.*, they would grasp the importance of getting rid of stop-cocks for nitroglycerin and using instead an india-rubber pipe. He might also refer to the necessity of preventing every sort of movable apparatus, especially things of weight, being in the workshops, and having everything that was possible fastened to the walls so that they could not be moved. Sir Frederick Nathan had reduced that to a fine art. Unfortunately, in his own department he had a large number of tools, gauges, etc., which could not be so fastened, but it was desirable that such arrangements as had been suggested should be made as far as possible.

Prof. **R. Meldola** thought that the investigation of the flocculent matter referred to in the paper as well as by the Chairman might throw some light on the course of chemical events. It might be due to the glycerin; and he asked whether it was used as it came from the makers; or, did it go through any process of purification? That seemed to be one of the independent variables they had not heard much about. He presumed that the quality of the commercial glycerin varied according to source, and it might introduce fluctuating elements which would have to be reckoned with.

Mr. **W. F. Reid** said not only had the improved arrangements introduced by the authors resulted in a reduction of risk to the work-people, but this had been attended with great economy. They knew that a yield of nitroglycerin of from 214 to 216 per cent. used to be considered very good, whereas they had now got to 229 per cent. or over.

The separation of nitroglycerin from the waste acids was first done by the Boutmy-Faucher process. Sulpho-glycerin was made by mixing glycerin with sulphuric acid, during which operation a certain amount of heat was liberated; and it was supposed that when this sulpho-glycerin was nitrated there would be a smaller evolution of heat and consequently less danger; but as a matter of fact the reverse was the case. There was such a slow separation of nitroglycerin from the waste acids that they frequently fired, and consequently the process had to be abandoned. The scum which formed between the nitroglycerin and the acids after nitrating was really a collection of vesicles; and when this was filtered through sand, a very small quantity of impurity was obtained in which he had found fatty acids, iron, and lead, but in what particular form they existed, and why they formed that particular vesicular structure between the two layers of liquid, it was difficult to say. He would be interested to hear from the authors whether they now frequently came across glycerin which caused trouble in nitration or separation. He believed that now the manufacturers of glycerin knew what was required so well that they produced an article much more regular in quality and safer than it used to be.

He had recently tested a number of glycerins of various origins, by nitrating in vacuum vessels, in order to measure the amount of heat produced, and had obtained some rather curious results; but he had not been able exactly to find out the particular bodies which produced these different results between glycerins which by the ordinary tests showed no difference whatever though there was a great difference in nitrating. In distilling glycerin no doubt some fatty acids passed over which were of the same boiling point, and when these were nitrated they were not so easily purified, and might produce unexpected results. With regard to the separation, in this plant he thought a most ingenious method had been devised for raising the whole body of liquid instead of skimming off or separating in a separating funnel. Many years ago he tried a method which worked very well, but he abandoned it for reasons partly connected with the safety of the work-people, and partly from difficulty in the mechanical arrangements; he lowered a vessel of lead into the liquid thus causing the latter to rise and the top layer flowed over a lip at the side. Possibly some modifications of that process might be utilised if there was any reason why fresh acid should not be added; but as this was usually not the case the method described that evening was one which ought to be adopted in every factory. He should like to ask with regard to the drowning arrangements whether the drowning tap had been often used, and whether there was a sufficiently rapid emptying of the charge to prevent over-heating.

Softening the water also eliminated a great danger. Sometimes guncotton or collodion cotton did not pass the heat test; this was no doubt often owing to the water used in the manufacture. As to the question of sodium carbonate in the nitroglycerin, Sir Frederick Nathan made a very pertinent remark with regard to its action on the flame, although he understood a certain percentage was considered necessary for it to pass the heat test.

Major Cooper-Key said that, although they did not call on manufacturers to have "Use lists" hung up in all the buildings on account of the expense, they would be exceedingly glad if they did do so, and he hoped the suggestion thrown out that evening might lead to their general adoption. Although the Home Office Inspectors did not insist on their being posted up, they acted in the spirit of the regulation by refusing to allow any article, either hard or heavy, to be present in any shed containing nitroglycerin.

Mr. R. B. Pollitt said he gathered that the authors considered that they could take the use of eight parts of mixed acid, and a yield of 216 per cent., as representing modern practice, for the purpose of comparing the latter, with Waltham Abbey practice, but he thought it was too high a ratio and too low a yield to take. He knew from practical experience, and no doubt many others knew it also, that it was quite possible to work with seven, or seven and a quarter, parts of mixed acid of ordinary composition, containing about 5 per cent. of water, to one part of glycerin and to obtain an average yield of well over 220 per cent. With regard to keeping the nitrating acid free from suspended mechanical impurities, it was surprising what a difference it made, not only in the rate and sharpness of the primary separation, but also in the amount of nitroglycerin that found its way to the secondary separators, and waste-water tanks. It was not difficult to prepare nitrating acid practically free from any suspended impurities, and the advantages gained much more than counterbalanced the slight extra cost involved. Working in the method referred to, and at a suitable temperature, secondary separators can practically be dispensed with, without adding water to the waste acid, and the amount of nitroglycerin-bearing "mud" collecting in the waste-water tanks is greatly reduced. The authors stated that they keep the temperature of nitration practically the same, winter and summer, but did not, he thought, say what it was, and it would be interesting to have the information. His own experience was that the temperature of nitration should be kept as low as it could be without risk of any of the nitroglycerin freezing on the coils.

Dr. R. Messel referred to his attempts, about 30 years ago, to introduce the use of fuming sulphuric acid in the explosive industry, partly for strengthening the mixed and waste acids, partly for obtaining an increase in the yield of trinitrocellulose, then the chief desideratum in the manufacture of guncotton. A real demand for this acid did not spring up, however, until the manufacture of nitroglycerin came more to the fore and it was shown that its use resulted in a not inconsiderable increase in the yield of nitroglycerin.

Mr. H. de Mosenthal thought that it would not be right to leave the impression that private factories did not work as advantageously as the Royal Gunpowder Factory at Waltham Abbey with regard to yields. As a matter of fact private factories obtained yields quite as good, if not better. The use of fuming sulphuric acid in the manufacture of nitroglycerin was introduced in Great Britain, France, Germany, Italy, Austro-Hungary, Russia, the United States, and South Africa several years prior to its introduction at Waltham Abbey.

Mr. Oscar Guttmann said the labyrinth had been devised by Mr. Alarik Liedbeck some 40 years ago, and he supplied improved drawings of it to Waltham Abbey. The sponge filter was used in the Boutmy-Faucher process, and illustrated in his book, and a similar one had been described in 1847. At the factory at Paulilles, a sponge used for wiping up nitroglycerin from the washing tank, on being left in the open air, fired, and since that time its use had been abandoned, therefore a sponge filter should be carefully attended to.

The Chairman said nitroglycerin manufacturers were at first only too prone to blame the glycerin. They rightly refused anything that did not comply with their requirements, but the glycerin makers had successfully fulfilled all their demands. It should, however, be pointed out that the nitroglycerin makers showed by their own specifications some curious notions as to possible impurities in glycerin. Thus they specified that glycerin must not curdle on passing nitrous acid through it, their idea evidently being that glycerin always contained oleic acid. This specification was still in vogue. In reality glycerin was nowadays delivered of such purity that it was the last thing the nitroglycerin makers could blame.

Sir F. Nathan, in reply, said the point which had been most frequently referred to in the discussion was the presence of flocculent matter in nitroglycerin. What it was, Mr. Reid had described, but how to prevent it, and why it occurred with some glycerins and not with others, were questions which although they had been worked upon for a considerable time, had not yet been satisfactorily solved. He was inclined to think however that it was not the difficulty it used to be. Dynamite glycerin manufacturers probably knew their business better than they did, and they certainly produced a glycerin which did not give so much trouble from this cause as it used to do. Again there was no doubt that now that, instead of its accumulating as a layer between the nitroglycerin and the waste acid as it did in the old form of separator; it came up and was removed with the nitroglycerin during the separation in the new form of nitrator-separator; it gave no trouble. It no doubt resulted from the presence in the glycerin of resinous substances, fatty acids and organic impurities, but ordinary chemical tests on glycerin as delivered in bulk failed to detect more of these substances in one sample than in others. The Chairman had asked if they knew anything about di-nitroglycerin, and tetra-nitroglycerin; he could only say they had devoted themselves entirely to tri-nitroglycerin, and so far had not done any work on either of those other forms. Di-nitroglycerin might have a future in connection with explosives, and several patents had been taken out recently for its preparation and use, but as he had no experience with regard to it he hesitated to express any opinion. It appeared to him, however, that there would be some difficulty in getting pure dinitroglycerin free from other nitroglycerines. He was happy to say, in reply to Mr. Reid, that during his sixteen years at Waltham Abbey they had never had occasion to drown a charge, but they did know that their arrangements would meet the case if unfortunately it became necessary. They had tested them, and knew that the rate of drowning wa[illegible]rly rapid, and they had the additional advantage that cold water was being added to the drowning tank along with the nitroglycerin and acid. As regards the average proportion of acid to glycerin being in practice 7 or 7½ to 1, their information rather tended to support the figure they had quoted of 8 to 1, which they believed was the figure used recently in most factories in this country, and in Germany. The glycerin before being used was submitted to all the usual chemical tests and to the nitration test, and that was not a laboratory one, because experience showed that laboratory nitration tests were fallacious as a guide to what would happen in manufacture. From every consignment of glycerin they received a drum was selected at haphazard and nitrated on the manufacturing scale, and only if it was satisfactory did they accept the consignment. For a long time now it had not been necessary to reject any consignment owing to its failing to pass this test. With regard to the labyrinth referred to by Mr. Guttmann, they had not been able to name the authors of all their improvements. The idea of the labyrinth was certainly suggested by Mr. Guttmann many years ago, though not perhaps for quite the same purpose for which it was now used at Waltham Abbey. Mr. Guttmann suggested that the labyrinth should take the place of the wash water settling tank and supplied a drawing of it as used at Hayle. They had rather extended the principle and put labyrinths in after every vessel from which washing waters were run, so as to trap as much nitroglycerin as poss[illegible] before it got down to the wash water settling house. He was glad to say they had not had any signs of any failure with the sponge filter.

Mr. W. **Rintoul** said a paper by H. Lemaître on the analysis of nitroglycerin waste acid (Monit. Scient., Dec., 1907), had recently come to his notice, in which it was suggested that the nitroglycerin present could be determined by extraction with chloroform. From the curves given in the paper, it would be seen that the result so obtained would be about 50 per cent. too low. Lemaître assumed that all the glycerin in the waste acid existed as a nitroglycerin in solution, whereas they had shown that this was not the case. The fall of the heat test of nitroglycerin on repeated filtration was probably due to the fact that the first traces of decomposition products were absorbed by the moisture and sodium carbonate present. Whatever the cause, the fact remained that, if nitroglycerin showing a high heat test was repeatedly filtered through paper, there heat test in all such cases fell, and in so regular a manner as to suggest that the heat test of pure nitroglycerin, carried out under standard conditions, was really constant, and that it was impossible to get pure nitroglycerin to stand a prolonged test.

Manchester Section.

Meeting held at Manchester on Friday, February 7th, 1908.

DR. J. F. THORPE IN THE CHAIR.

SOME APPLICATIONS OF THE "CLARIFICATION TEST" TO SEWAGE AND EFFLUENTS.

BY GILBERT JOHN FOWLER, D.SC., F.I.C.,
SAM EVANS, B.SC. (TECH.), AND ARTHUR CHADWICK ODDIE.

Introduction.—In a paper read before this Society in May, 1905,(¹) attention was drawn to the importance of determining the proportion of the suspended matter in sewage and effluents which is present in the colloidal state, or in a state of fine division or emulsion, as this constitutes potential solid matter which has to be ultimately dealt with. Reference was made to previous work on the subject (²) and a number of results were given, obtained by submitting samples of sewage from various sources and of sewage and septic tank effluent, to dialysis in parchment cylinders. The importance of the subject has been since fully recognised, and numerous papers (³) have appeared dealing with various aspects of the question.

The object of the present paper is to record a number of results which have been obtained by precipitation of the colloidal and finely suspended matters by means of basic ferric acetate, a method originally suggested by Rübner, (⁴) and mentioned by Fowler and Ardern in the paper already referred to, (⁵) which, for the sake of brevity, is here spoken of as the "clarification test." This method has been found to yield as instructive results as the method of dialysis, while it occupies much less time, and probably, in consequence, is less liable to error.

Clarification test.—The method adopted is as follows:—To 200 c.c. of the sample in a conical flask are added 2 c.c. of a 5 per cent. solution of sodium acetate and 2 c.c. of 10 per cent. ferric ammonium alum solution, the whole shaken and placed over a Bunsen burner. Immediately the liquid begins to boil the flame is turned down and the liquid kept just on the boil for two minutes. It is then removed, cooled under the tap, and filtered, introducing as little of the precipitate on to the paper as possible. In this way a clear filtrate is obtained which, therefore, may be taken for practical purposes to contain only substances in "true" solution. The filtrate is then analysed and the results compared with those obtained before clarification.

The precise period and method of boiling were chosen after a number of trials as being those which allowed no more liquid to be evaporated than was equal to the volume of the reagents added, the concentration of the sample is thus unaffected by the clarification. A number of blank experiments showed that, at any rate in dealing with sewage and effluents, the errors introduced by the addition of reagents and by the use of ordinary filter paper were inappreciable, especially as the chief value of the test lies in its use as a rapid method of comparing a number of samples, any small error therefore being common to all.

The exact method of estimating the amount of oxidisable matter present in the unclarified and clarified sample is a matter of more importance. It was at first thought that boiling with acid permanganate and titrating with oxalic acid, generally known as the Kubel method, would

---

(¹) G. J. Fowler and E. Ardern, "Suspended Matter in Sewage and Effluents" (this J., 1905, 483).

(²) Manchester Corporation Rivers Committee, Annual Report for Year ending March, 1901, pp. 40—41. O. Kröhnke and W. Biltz, Hygien. Rundschau, 1904, 9. Ber., 1904, 1745. (This J. 1904, 619.)

(³) A. S. Jones and W. O. Travis, Proc. Inst. Civil Eng., 1905—1906, Paper No. 3599. F. R. O'Shaughnessy and H. W. Kinnersley, this J., 1906, 719. J. H. Johnston, J. Roy. Sanitary Inst., 1906, 548. J. W. Ellms and J. F. Snell, Zeits. angew. Chem., 1906, 35. W. Biltz and O. Kröhnke, Cer. Ing., 1907, 350. (This J. 1907, 711.) W. O. Travis, Contract J., Dec. 11 and 18, 1907.

(⁴) M. Rübner, "Das Städtische Sielwasser und seine Beziehung zur Flussverunreinigung." Archiv. für Hygiene, 14.

(⁵) *Loc. cit.*