and other chemists, involving a variety of modes of standardization.

The merits of the Zimmermann-Reinhardt method may be summed up as follows: (*a*) That the liquid resulting from the solution can be treated directly and without the use of special apparatus. (*b*) The operation of titration is not tedious as in the bichromate method. (*c*) That the simplicity of operation permits determinations to be made with rapidity[1] and without sacrifice of accuracy.

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ON THE MANUFACTURE OF SOLUBLE NITROCELLULOSE FOR NITROGELATINE AND PLASTIC DYNAMITES.[2]

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THE discovery that a nitrocellulose could be prepared, which was soluble in a mixture of ether and alcohol, other light hydrocarbons, and in nitroglycerol, gave a start to several industries, of which not the least important was that of the manufacture of nitrogelatine, discovered by the Swede, Alfred Nobel. The use of this substance in the production of celluloid, etc., is of great importance to the industries of this country, but falls outside of the scope of this article.

In order that nitrocellulose should be easily soluble in nitroglycerol it ought to be, as nearly as possible, a pure trinitrocellulose. Higher nitration degrees are insoluble in nitroglycerol, a lower one is fully as unsatisfactory in its action and, therefore, the preparation of this substance is considered one of the most difficult problems encountered in the explosive industry. It is, in fact, considered so difficult to produce, that its manufacture is avoided by explosive companies, they preferring to buy the collodion-cotton made for celluloid manufacturing, at a high

[1] In ordinary practice in our laboratory, determinations can be made in five to ten minutes after the ore is weighed out.

[2] Read before the Washington Section, March 14, 1895.

price, in place of running the risk of a failure in manufacturing their own nitrocellulose, although if successful it could be made at a much lower cost.

As a matter of fact, the process of its manufacture is not difficult nor does it require any great chemical skill, but it does require great care in manipulation, uniformity of the materials used, and a never ceasing watchfulness of the details. The cellulose used for its preparation need not be the pure cotton used in the celluloid industry. The inferior article, known in the market as cotton-waste, is quite suitable for this purpose. To be sure the pure cotton is somewhat easier treated and requires less care in the composition of the acids used, but the difference in price between this article and the cotton-waste more than compensates for the additional handling and care. The cotton-waste must, of course, not contain too much fatty matter, but small amounts of organic acids are quite allowable as they are easily removed by suitable washing before using. To do this the bale of cotton-waste is placed in a wooden tank (cedar or best pine wood). I have found that a tank three feet high by five feet in diameter is a convenient size for this purpose. It is now washed, first, with hot water, then with a caustic soda (or sal-soda) solution, about two and one-half pounds caustic soda to a tank full of water, and again thoroughly washed with running hot water. The water having been drawn off, the cotton is taken out and dried, either by hydraulic pressure or by passing it through a centrifugal machine. It is then placed in drying rooms at a temperature of from 75° to 90° C., for at least two days, or until every particle of moisture is driven out. The next process is to pick the dried cotton into a fine fiber. For this purpose a number of cotton-picking machines are constructed and put on the market. They all possess some merits and are indispensable to a large manufacturing plant for nitrocellulose, but require capital to introduce and skilled labor to run, whereas, on the other hand, "hand-picking" is quite satisfactory, does not require initial capital, and labor otherwise wasted can easily be employed. In trying both machine-picking and hand-picking, I have found that the latter gives a more uniform result, and that (on a smaller scale at least) the time of the men waiting

for the nitration of a previous batch can be profitably used for this purpose.

As is always the case, when a number of nitro-derivatives can be obtained simply by using a stronger or weaker nitric acid and by changing the conditions under which it is used, the tri-nitrocellulose can be obtained in several different ways. The factors to take into consideration are:

(1) The *proportion* of sulphuric and nitric acids used in the mixture.

(2) The *strength* of the two acids respectively.

(3) The *length of time* the acid mixture is allowed to be in contact with the cotton.

(4) The *temperature* maintained during the reaction.

(5) The *construction* of the plant itself; and a number of minor conditions, such as the humidity of the atmosphere at the time of the reaction.

In addition to this, there is to be taken into consideration in life, outside of the laboratory, such important items as the cheapness of plant, saving of time and economy of labor. To thoroughly investigate and finally bring each one of these conditions into such harmony that the best and most uniform product at the least expense can be produced is, in itself, a life-work and has not so far been accomplished. I will simply indicate the importance of each one of these questions and then describe *one* way, which I have found, after numberless experiments, to give satisfaction; that is, to produce a nitrocellulose soluble in nitroglycerol at a reasonable cost.

If too *much* sulphuric acid be used this is likely to attack the cotton *before* the nitric acid begins to act, converting it partly into cellulose hydrate (this will later be converted into a higher nitration degree by the nitric acid, as it is much more readily acted upon than the cellulose and will then form an insoluble nitrocellulose) and partly into glucose, which will again partly be nitrated to nitrosaccharose, which is insoluble in nitroglycerol and, besides, a very dangerous substance to have present. Again, if too *little* sulphuric acid be present it will soon form its highest hydroxide and be unable to absorb more of the water rapidly formed during the reaction, when the nitric acid will

become diluted and be unable to nitrate the cellulose. The right proportion of acid mixture is, therefore, of great importance.

If *too strong* sulphuric acid be used the result will be the same as above mentioned for an excess of it; if too strong, or too weak nitric acid be used, it is obvious that a higher or lower nitration degree than the one desired will result. It goes without saying, therefore, that the strength of the acids are of utmost importance.

In the reaction between nitric acid and cellulose no fumes are given off, except what is driven off by the heat (in which it widely differs from several other nitration processes) and although the reaction becomes feebler and, eventually, completely stops, when the acid has been diluted to a certain limit, it only gradually diminishes in force, and therefore the time has to be so balanced that the lower nitration degrees have been passed without part of the cellulose having been too highly nitrated, when it is stopped. Hence the importance of careful regulation of the time.

If the nitration pots are surrounded with water kept at a constant temperature, it will be found that the quickness and degree of the nitration depends, to a considerable extent, upon the temperature of this water. Thus, if the temperature be kept up to a high degree the nitration will be much more rapid, but at the same time experience has shown me that, in this way, a *mixture* of different nitration degrees is much more apt to result, than the uniform nitration from one degree to another. Curiously enough, the same result is obtained if no external heat at all be applied, and accordingly in my experience a carefully maintained temperature of 70° C. has been found to give the most uniform result, but no doubt good, and perhaps more economical results can be reached by elevating the temperature of the surrounding water.

It is within the experience of every chemical manufacturer, how much the size and construction of the vessels, in which the reaction takes place, influence the result, and this is fully as true in this industry as in any other. It is especially so as the cotton is so bulky that it is hard to keep every part of it in contact with the acid mixture. Under otherwise the same conditions, I have found quite a difference in the product when it was made on a

clear and dry day, and when the day was rainy or cloudy, the more so, as the building in which the operation takes place has to be left open to a great extent to allow the acid vapors to be carried away.

Even in very large dynamite works it is not always practicable to adopt the very best appliances for the manufacture of nitrocellulose, because it must necessarily be only a small part of the plant (an average of two per cent. of the ingredients) and can only be conducted by dependence for labor, material, etc., on other parts of the works. In a large plant for the exclusive manufacture of this kind of nitrocellulose the conditions would be more favorable for improvements.

The acid mixture I have found best to use is the following: Nitric acid of 1.430 sp. gr., free from chlorine and such an amount of sulphuric acid as would influence the specific gravity, forty parts; and sixty parts of sulphuric acid of 1.835 sp. gr. The specifications for acids governing the supply for other parts of the works can be adopted for this. It is self-evident that this proportion of acids is only necessary when the work is carried on as hereinafter described and can be greatly varied under different conditions. Such an acid mixture as this cannot be stored in iron drums for any length of time and is therefore troublesome to get, if the nitric acid is not manufactured at the works. The nitric acid must be shipped in carboys; the sulphuric acid can be shipped in drums.

In mixing the two acids a sufficient quantity can be mixed at one time to last for two or three days' supply, and then stored in drums, as the acid will hardly, in this short time, affect the iron to any great extent. The mixing is best effected in a wooden tub lined with heavy lead in such a way as to allow a water-jacket of about two inches around it. (A condemned nitroglycerol apparatus with the coils removed answers this purpose very well.) If compressed air be at hand this should be used as a stirrer by placing a small perforated lead coil at the bottom of the tank and letting the air bubble through the mass since it is very difficult to get any other kind of stirrer that will stand the acids. The men should be warned to have the earthen-ware faucet at the bottom of the tank well greased, to tap it very

gently, to always use their rubber gloves and to have an ample supply of water close at hand.

This mixture although carefully made from acids of 1.430 and 1.835 sp. gr. respectively, will vary in specific gravity from 1.678 to 1.682, but if below or above this, some mistake has been made in the mixing or stirring. The nitric acid should always be dumped in the tank first and the sulphuric acid afterwards so as to give the latter a chance to mix by gravity as much as possible. Just before using, the acid mixture should be stirred again. For this purpose it is convenient to have a lead-lined tank, with an air-stirrer, of a size to hold one charge for the nitrating pots in use, in which the mixture is stirred up thoroughly and then drawn off for each pot as rapidly as possible.

The arrangement of the nitration pots, of course, must depend on existing conditions, such as size and form of the building, the size of the pots, the material used for confining the water around them, the supply of water of suitable temperature, etc. Under ordinary circumstances I have found it practicable to use earthenware pots sixteen inches deep and thirteen inches in diameter, enclosed in wooden troughs twenty feet long by twenty inches wide, connected by means of leaden pipes. If shorter it is a waste of lumber, if longer they are likely to leak from the pressure. If the troughs can conveniently be made from concrete or brickwork with water-tight mortar, of course it can be extended to any desired length.

Experience has shown two pounds to be the right amount of cotton to be used in one nitration pot. To save time and labor it is important to nitrate as much as possible at one time, but the necessity of getting a uniform product limits the amount, and as the cotton clogs or packs together as soon as wet by the acid mixture, only so much can be used at one time as will allow the mixture to act uniformly on the whole bulk of the cotton, without nitrating the outer portion too much and the inner portion too little. After having tried different amounts I have reached the conclusion that (under the given conditions) two pounds is the maximum that can safely be treated in one nitration pot.

Forty-five pounds of the well-stirred acid mixture is weighed

out and placed in the pots, which are surrounded by water heated to 70° C. The two pounds of cotton for each pot should be previously weighed out, and ready to be put in so as to have this done as nearly simultaneously as possible. It is now immersed in the acid mixture, turned about a few times with a fork and kept down by a perforated cover. The only reason for using such an excess of acids is that the cotton must be covered by it—if good covers are used forty pounds or less is enough. Besides the perforated covers, each pot should be provided with solid overlapping covers to keep back the fumes. It is now left for one hour and ten minutes, except that after thirty-five minutes the cotton is quickly turned about with the fork, a couple of times and the covers replaced. After this the nitrated cotton is quickly taken up, squeezed with the fork, and wrung out in a centrifugal machine. From this it is taken to a large-sized tank well filled with cold water, where it is thoroughly washed. It should be kept in this tank in running water for about one hour. It is well to have a large quantity of water to prevent heating by adherent sulphuric acid, but it is not so important as in the case of guncotton, because it is not so easily ignited by the heat generated nor is the acid as strong as in the latter case. It is then transferred to another tank of the same size. This is conveniently placed below and the nitrocellulose transferred on a wooden slide. Here it is washed in a sal-soda solution. From this it is taken to a pulping machine or hollender, where it is reduced to a fine pulp. This part of the process is of the greatest importance as it has been proven time and time again that if insufficiently pulped it is hard if not impossible to dissolve it in nitroglycerol. I have found that nitrocellulose, which had before been rejected as insoluble, worked very well after it had passed two or more hours in the pulp-machine. From the pulp-machine it is emptied into a large tank, allowed to settle, and the water filtered off. It is then passed either through a centrifugal machine or a hydraulic press, and thus freed from water as far as possible. It is spread in drying boxes to a depth of about two inches and kept at a temperature of about 80° C. till thoroughly dried. After that it is rubbed through fine screens until as fine as the finest flour. If treated in this way the nitrocellu-

lose will dissolve very quickly in nitroglycerol. Seven per cent. of nitrocellulose dissolves in ninety-three per cent. nitroglycerol in less than twenty minutes to a transparent jelly and three and five-tenths per cent. gives the nitroglycerol the consistency of syrup. Several hundred analyses of nitrocelluiose prepared in this way show it to contain from 20.5 to 21.8 per cent. of NO_3, which very nearly corresponds to the formula of trinitrocellulose. The process carried out in this way is simple and requires no great skill or experience. The cost under ordinary circumstances and with conscientious supervision varies between thirty-five to forty cents a pound. The spent acid must of course be taken care of either by regaining it or by using it direct for other chemical processes. The only laboratory facilities that are absolutely needed are three different hydrometers, one thermometer, and a specific gravity jar—provided the acid contractors are honest.

If the nitric acid be made at the works there is no difficulty in economizing by using the lower grades made up to strength, from the acid for nitroglycerol manufacture, for instance, or from other high grades. If properly and constantly tested the waste nitroglycerol acids can be made up to strength if sufficiently strong nitric and sulphuric acids are on hand. A good and attentive chemist is certain to be able to use the products from other parts of the works (nitroglycerol works, regaining works, acid works, etc.), in such a way as to accomplish a considerable saving in the price above quoted of nitrocellulose. The conditions and facilities for making it differ, but it is safe to say that the makers can save from ten to twenty-five per cent. of the cost of manufacture in the above way by the employment of a competent chemist, to say nothing of what they save by not buying the collodion-cotton of the market at $1.00 a pound.

The best way to test the nitrocellulose for efficiency in the laboratory is undoubtedly by trying its solubility in nitroglycerol under the same conditions as prevail in the works, next to that is to note the time and result in dissolving it in an ether-alcohol mixture, and finally to use Lunge's nitrometer. The last test, though of less direct practical value, will enable the chemist to obtain a pretty good idea of what he is making and a well-

kept record of all these tests is sure to soon make it possible to always turn out a uniform product—the great desideratum in all chemical industries. The laboratory method of testing, and analysis of materials for, and products of this industry are so simple that they need not be mentioned to an assembly of chemists.

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NEW BOOKS.

ELEMENTS OF QUALITATIVE AND QUANTITATIVE CHEMICAL ANALYSIS. By G. C. Caldwell, B.S., Ph.D. Third Edition, Revised and Enlarged. pp. 187. Philadelphia: P. Blakiston, Son & Co. Price, $1.50.

Dr. Caldwell has made several changes in this third edition which increases the value of a book which already had much to recommend it, as the writer can testify, having used it in the laboratory for two years. Nitroso β-naphthol is added as an additional test for nickel and cobalt. It would seem as though more tests might be added for the basigens, with advantage to the student. On page 15, the equation for the oxidation of oxalic acid by potassium permanganate is not correct in this, as it was not in the former edition. The marks ⌣⌣, ⌢⌢, to indicate respectively "precipitate" and "gaseous product," so far as we know entirely original with the author, are great aids to the instructor in the class-room drills. The discussions in Part I on the processes of analytical chemistry are particulary valuable, while the preliminary discussions preceding the schemes, on "the chemistry of the work" are an excellent feature. Lawrence Smith's method for alkalies is added in this edition. While the portion devoted to quantitative analysis is necessarily abbreviated in a work of this character, sufficient space is given to allow students of limited time to get a very good general knowledge of the methods employed. But we would like to have seen the determination of potash added to those of phosphorus pentoxide and nitrogen, for those interested in agricultural analysis.

ALBERT H. WELLES.

ELEMENTARY QUALITATIVE CHEMICAL ANALYSIS. BY FRANK CLOWES, D. Sc. LOND., AND J. BERNARD COLEMAN. pp. 180. Philadelphia: P. Blakiston, Son & Co. Price $1.00.

The reviewer fails to discover any important improvements in the arrangement or matter in this book upon others of the same