VOL. XXIII. [AUGUST, 1901.] No. 8.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

RESEARCHES ON NITROCELLULOSE.

BY G. LUNGE.

Received June 26, 1901.

CONTENTS.

INTRODUCTION.

The work reported in the following pages has been carried out during the years 1897 to 1900, the first part with the cooperation of Dr. Weintraub, the second with that of Dr. Bebie.[1] In the description which I shall give of these researches, I shall not adhere to their chronological sequence, but group them in their logical order, the later researches being sometimes only confirmatory or supplementary to some carried out at a previous stage, and sometimes modifying the conclusions previously arrived at. This present report consequently affords a clearer picture of the ultimate results of our work than the separate German publications, and embodies also a few facts that later came to my knowledge.

The object of this investigation was to study the conditions under which nitrocelluloses of various composition and various properties can be regularly and with certainty prepared, and to establish both the composition and the properties of the products obtained under varying circumstances with greater accuracy than had been done up to that time, as witnessed by the considerable discrepancies among the statements of different authors.

My ultimate object was to try whether the technology of nitrocelluloses could not be advanced somewhat more beyond the classical researches of Sir Frederick Abel than had been done by the various publications of subsequent authors, meritorious as these are, especially as their opinions differ in important matters, and sundry points of great moment had not been at all elucidated.

It is hardly necessary to say that I cannot pretend to approach the unique work of Abel, if for no other reason, because the work of my cooperators and myself was confined to the resources of a well equipped laboratory, whereas he had an opportunity of testing his results on a large scale, and thereby, as all the world knows, laid the foundation of the present industry of guncotton. Nor is it necessary to say that very possibly similar work to that which we have carried out at Zurich may have been done in the secrecy of factory laboratories, and the result applied to practice. Of this secret work, if such has been done, I have absolutely no knowledge, nor is it the property of the industrial world in general, and the science of technology is thereby no more benefited than are the interests of other manufacturers than those for whom it has been specially undertaken. I make this remark in view of the

---

[1] Compare the former with: *Ztschr. angew. Chem.*, 1899, pp. 441 and 467; the latter is in course of publication in the same *Zeitschrift*.

possibility that after my publication somebody may say that this or that part of my results has been already known to him. Such *private* information should not debar others from pursuing the path of knowledge in the general interest of science and industry. But I am not aware of any such work having been done privately on the same lines as ours, and I can only deal with what is to be found in literature.

I. GENERAL REMARKS ON THE METHODS EMPLOYED FOR NITRATING CELLULOSE.

The material employed throughout the work (except for the special purpose described in Section III, *I*), was the so-called "chemically pure surgical cotton wool." In order to remove the last traces of fat, it was boiled for some time in a weak solution of sodium carbonate, well washed with water and extracted with alcohol and ether. The percentage of ash found = 0.06 per cent. on the average of several estimations. Immediately before nitration the cotton wool was dried at 100° till the weight was nearly constant, allowed to cool in the desiccator, and at once placed in the nitrating vessel.

The acid mixtures were made from weighed quantities of "chemically pure" sulphuric acid (sp. gr. 1.84) and fuming nitric acid (sp. gr. 1.52). The former as used for the first part of this work showed an analysis of 95.62 per cent. H_2SO_4, the latter 93.76 per cent. HNO_3, and from 1 to 2 per cent. lower oxides which were removed in the ordinary way. For the second part of the work, where more particular attention was paid to the exact percentage of water present, the mixture was always analyzed when complete, and its exact composition is stated in the respective sections.

For carrying out the nitrations the apparatus shown in Fig. 1 was employed. A stout cylindrical jar, *A*, was closed by means of a tightly ground-in glass cover, *B*, provided in the center with a drop-funnel, *C*, and on one side with a tube, *D*, bent at a right angle and closed by a glass tap, both of them sealed to the glass cover *B*. The latter was further perforated for admitting a thermometer, *E*, which was fixed perfectly tight by means of asbestos and sodium silicate solution.

The cellulose was placed in the jar, the cover put on, and the acid mixture poured into the drop-funnel. The lateral tube was connected with a good Bunsen pump, and nearly all the air was thus removed from the jar and the cotton wool. Now the connection with the Bunsen pump was shut off, and the acid slowly run in from the drop-funnel. For nitrating at higher than the ordinary temperatures the acid mixture was heated a little above the desired temperature, placed in the drop-funnel, and after cooling down to the proper point, run on the cotton. The temperature within the vessel was regulated by placing it in a large water-bath. Sometimes, in the case of operations taking a long time and going on over night where temperature observations were impossible, the described apparatus was replaced by ordinary wide-mouthed jars with ground-in stoppers.

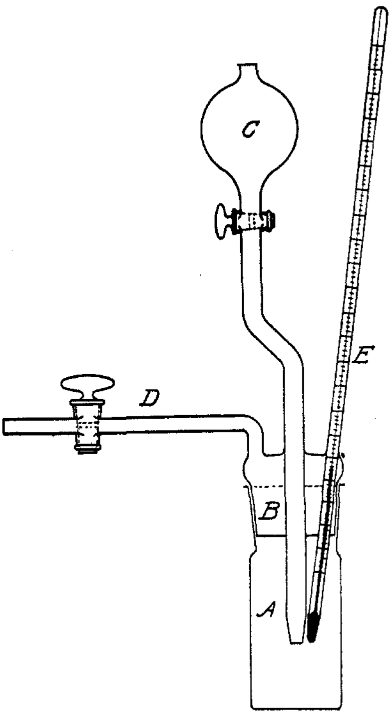

Fig. 1.

When the action of the acid had lasted sufficiently long it was separated from the nitrocellulose first by decantation and secondly by the action of the vacuum pump, employing a porcelain funnel with porcelain sieve. The mass was placed in cold water and quickly moved about in order to avoid any considerable rise of temperature. The washing was performed first with cold, then with hot, water, and before each renewal of the water the nitrocellulose was again freed from liquid by means of the vacuum funnel.

The washing requires various lengths of time, according to the physical structure of the nitrocelluloses,—usually two or three days. Later on we shall describe the washing processes employed in special cases.

The mode of operation just described could be employed only in those cases where the nitrocellulose retained a structure similar to that of the cotton fiber. When employing acid mixtures containing a large excess of sulphuric acid, this structure is destroyed; this product consists of short fibers, suspended in the liquid. In this case, after the nitration has been completed, the whole was poured into an excess of ice-water and then filtered through a porcelain funnel whose sieve-plate was covered with linen or filter-paper. The nitrocellulose was then washed by decantation in a large Erlenmeyer flask.

After washing, the nitrocellulose was dried either in a vacuum-desiccator protected against light or else in a special apparatus shown in Figs. 2 and 3, by means of a current of dry air at a temperature of 40° in the earlier, or from 30° to 32° in the later experiments, (the latter temperature having been found to be sufficiently high). For this purpose the product was placed in a cylindrical glass vessel, *A*, contracted at the bottom into a tube *a*, bent at a right angle. Just above the concentration a porcelain sieve, *b*, is placed, on which the nitrocellulose rests. The top is closed by a ground-in glass cover, *c*, with a lateral tube, *d*, and a hole in the center for a thermometer reaching *e* down to the substance. Usually two sets of apparatus were employed at the same time by connecting the inlets *a* with a T-tube supplied with air dried by calcium chloride and sulphuric acid. Both vessels, *A*, were placed in an asbestos box, *B*, whose bottom was heated by a very small gas-jet. The four sides of the box were made from a piece of asbestos cardboard, cut half through lengthwise and bent round to form a square tube, the last edge being formed by

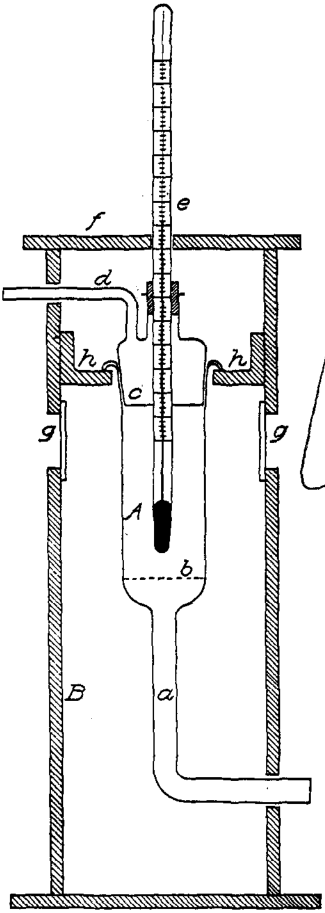

Fig. 2.

means of iron wire clamps and strengthening all the joints with asbestos paper soaked in water-glass solution. The cover *f*, also made of asbestos, is movable and is perforated for the passage of the thermometer *e*. Tube *A* is suspended by means of small glass lugs on the edges *h h*. One of the sides of the box *B* has two openings near the bottom for the air-supply pipes *a* and another side has openings for the air-escape pipes *d* near the top; half way up, at the level of the nitrocellulose, there are small glass windows *g g*, opposite each other which allow of observing the process. The box is placed on an asbestos plate, and by means of a small gas-jet the temperature can be kept constant to 0.5° or at most 1° during several hours, while air, which has passed through calcium chloride and sulphuric acid, is passed in at *a* and passes out at *d*.

This asbestos oven, which it takes about an hour to construct, has done us excellent service. It admits of drying the nitrocellulose in a current of dry air at the desired temperature which is attained within the asbestos box in contact with the glass vessel. On the large scale, of course, the air would be previously heated to the requisite point; but this is very difficult to attain with any degree of accuracy in a laboratory apparatus and is quite unnecessary, when using the arrangement described.

The exit-tube *d* is connected with a flask containing concentrated sulphuric acid, in order to retain any nitrous vapors evolved from the nitrocellulose during the drying process.

This apparatus effects a very great saving of time as compared with drying in the desiccator. Nitrocellulose carefully freed from water by pressing requires seven or eight days' drying in the desiccator, but only twelve to fifteen hours in the asbestos oven, to attain constancy of weight. Check tests made of the same sample of nitrocellulose with both modes of drying never showed any appreciable difference in the nitrogen percentage. A very slight loss of nitrous vapors, however, does take place, although unappreciable by the most careful analysis of the product, for the sulphuric acid through which the exit air was passed usually destroyed two or three drops of decinormal permanganate. Therefore in more important cases the slower, but absolutely certain, method of drying in the desiccator was preferred.

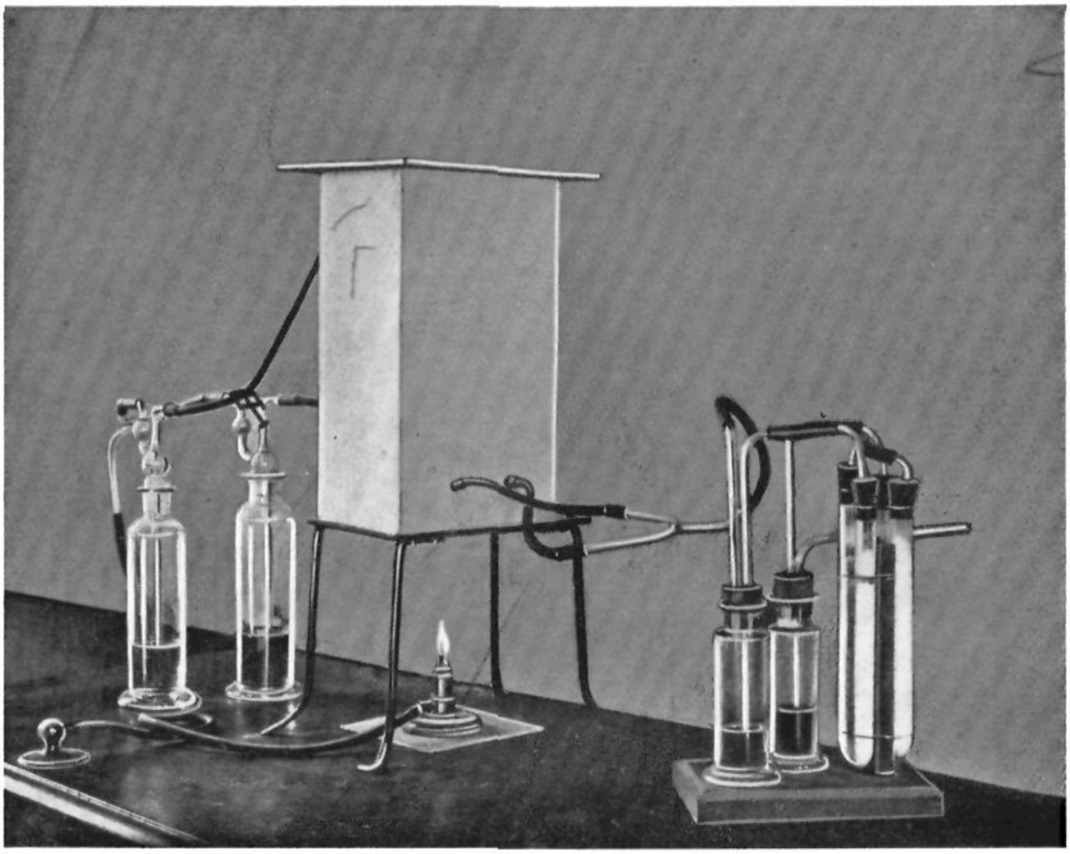

Fig. 3.

II. ANALYTICAL METHODS.

A. The Estimations of Nitrogen were always performed in my well-known gas volumeter (five-part nitrometer). The nitrocellulose was dissolved in concentrated sulphuric acid in the funnel of the agitating-vessel, provided with a rubber stopper and swan-neck tube; only the short fiber products which cannot easily be put into the funnel without loss by dusting were dissolved in a stoppered weighing-bottle. Usually the solution was effected in from half an hour to an hour; exceptionally the close quality of a product caused it to be very slowly penetrated by the acid, in which case the operation lasts up to twenty-four hours. The results are exceedingly accurate; the difference among various estimations is rarely more than 0.1 to 0.2 cc. NO per 1 gram, which means about 0.01 per cent. nitrogen.[1]

Williams[2] asserts that, if the nitrometer funnel is rinsed first with concentrated and afterwards with slightly diluted acid, the results are 0.2 per cent. higher than when using concentrated acid alone, owing to the rise of temperature produced in the former case, which is necessary for completing the decomposition. This assertion is not correct, as was shown by very careful estimations, in which the same sample was tested (1) by rinsing with concentrated acid only and (2) by employing dilute acid at the end:

	Nitrogen. Per cent.	Nitrogen. Per cent.
(1)	13.30	13.28
(2)	13.27	13.29

We tested also Chenel's method,[3] which is a modification of Kjeldahl's method. The results were satisfactory, but this method is far more troublesome and lengthy than the nitrometer method, so there is absolutely no reason for preferring it to the latter which is at least equally accurate.

The English and German way of stating the results is to quote the percentage of nitrogen; in France the results are stated as the number of cubic centimeters NO (reduced to 0° C. and 760 mm. pressure) evolved by 1 gram of the substance.

$$15.95 \text{ cc. NO} = 1 \text{ per cent. N};$$
$$1 \text{ cc. NO} = 0.0627 \text{ per cent. N}.$$

---

[1] The difference between the atomic weights ordinarily used in calculations (O = 16, N = 14, C = 12, H = 1), and the exact atomic weights (O = 16, N = 14.04, C = 12, H = 1.008) amounts to more than the above discrepancies.

[2] *Moniteur Scientifique*, 1899, p. 920.

[3] *Mém. des poudres et salpêtres*, **8**, 45.

To facilitate comparisons I append the following table, calculated with the exact atomic weights accepted by the German Chemical Society.

TABLE I.

Degrees of nitration.	Formula.	Nitrogen. Per cent.	NO per 1 gram. cc.
Dodecanitrocellulose (= old trinitrocellulose)	$C_{24}H_{28}O_{20}(NO_2)_{12}$	14.16	225.53
Endecanitrocellulose	$C_{24}H_{29}O_{20}(NO_2)_{11}$	13.50	215.32
Decanitrocellulose	$C_{24}H_{30}O_{20}(NO_2)_{10}$	12.78	203.87
Enneanitrocellulose	$C_{24}H_{31}O_{20}(NO_2)_9$	11.98	191.08
Octonitrocellulose (= old dinitrocellulose)	$C_{24}H_{32}O_{20}(NO_2)_8$	11.13	177.52
Heptanitrocellulose	$C_{24}H_{33}O_{20}(NO_2)_7$	10.19	162.53
Hexanitrocellulose	$C_{24}H_{34}O_{20}(NO_2)_6$	9.17	146.26
Pentanitrocellulose	$C_{24}H_{35}O_{20}(NO_2)_5$	8.04	128.24
Tetranitrocellulose (= old mononitrocellulose)	$C_{24}H_{36}O_{20}(NO_2)_4$	6.77	108.01

In the original papers the results are generally stated in cubic centimeters NO, but as this is less familiar to Anglo-American readers, I have translated them all into nitrogen percentages.

In the first series of experiments (of which there were several hundreds performed) the *yields* were regularly determined; later on this was only occasionally done, as this repetition seemed unnecessary.

B. Wherever *the solubility in ether-alcohol* had to be determined, one of the two following methods was followed: Where only a few per cent. of soluble matter is present, this can be extracted by ether-alcohol, and the insoluble residue dried and weighed. This process does not answer where there is much soluble matter present, because in this case the solution is too viscid and too difficult to filter and the residue too gelatinous for proper washing. In these cases the English method was employed: Treating the substance in a stoppered cylinder with a certain quantity of ether-alcohol, allowing to settle, withdrawing a portion of the clear supernatant liquid by means of a pipette, evaporating and drying at 50° till the weight is constant. By this process the soluble nitrocellulose is converted into a tough compact mass which it is very difficult to entirely free from the solvent; hence the results are too high; in the case of perfectly soluble nitrocellulose usually 102 or 103 per cent. was found. Better results were obtained by precipitating the nitrocellulose from the solution in a flocculent form by careful addition of water before evaporation, with constant stirring, until a permanent turbidity was produced.

The solvent usually employed was a mixture of three parts ether (sp. gr. 0.72) and one part alcohol (sp. gr. 0.81), but we shall see in Section III, *G*, that the same results are obtained by many other proportions of these ingredients.

C. The Analysis of the Acid Mixtures was performed according to the methods described in my "Taschenbuch für Sodafabrikation" 3rd edition, p. 249. (This is a somewhat enlarged and improved form of the methods given in Lunge and Hurter's "Alkalimaker's Handbook," 2nd edition, p. 155.)

D. Examination of the Nitrated Celluloses under the Polarization microscope.—The statements found in literature on the behavior of nitrocelluloses in polarized light show great discrepancies. In Muspratt-Stohmann's Chemistry (1869) it is stated that guncotton, when observed under the microscope in polarized light, exhibits no, or almost no, color, whereas cotton fiber shows bright and beautifully variegated colors. Morton Liebschütz (*Moniteur Scientifique*, 1891, p. 119) says that the compound which he calls hexanitrocellulose (our dodecanitrocellulose) can be recognized by its greater brilliancy and slate-gray color; penta- (our deca-) nitrocellulose by its blue color; tetra- (our octo-) nitrocellulose by its yellow color. Guttmann[1] says: "If examined under the microscope with polarized light, ordinary cotton is colorless while guncotton exhibits colors." This is a clerical error, as stated by Guttmann in his contribution to my "Chemisch-technische Untersuchungsmethoden," Vol. II, p. 477. Chardonnet[2] makes the following statement: Up to 6.9 per cent. nitrogen the nitration can be recognized only by a few large, shrunk-up fibers; from 6.9 to 9.1 per cent. nitrogen there are more such fibers, and a few rainbow-colored ones; from 9.15 per cent. on the fibers turn more evenly gray; from 10.0 to 11.28 per cent. they turn straw-colored to orange; above 11.28 per cent. nitrogen the fibers appear first colorless, afterwards purple, dark blue, and light blue, the last color becoming prevalent as the nitrogen increases. When all fibers are equally light blue, the action is finished.

The continued observation of our products, along with their

---

[1] "Manufacture of Explosives," Vol. II, p. 59.

[2] According to Wyss-Naef: *Ztschr. angew. Chem.*, 1899, p. 31.

careful analysis, has led to the following conclusions which I believe to be quite correct. The most highly nitrated products show in polarized light a blue color. These products, whose nitrogen percentage varies between 13.9 and 13.0, cannot be distinguished from each other by polarization. As the nitrogen percentage rises, the blue color becomes less intense, but decidedly never turns slate-gray or colorless. Certainly some gray fibers can be observed here and there, but not in proportion to the increase of nitrogen. On the contrary, the highest degrees of nitration (13.9 per cent. nitrogen) appeared almost purely blue, and in products of only 13.0 most fibers were gray, although there was always a mixture of both present, and it was observed that on turning the object table, gray fibers flashed up in a blue light and *vice versa*, that is to say, the blue color appears in a certain position, and the gray color in another.

The purple transition shade mentioned by Chardonnet could not be observed. From 12.4 per cent. downwards most fibers showed a gray luster which, when keeping off the top-light, mostly turns faint yellow, but sometimes remains unchanged. This goes down to 10.66 per cent.; below 10 per cent. nitrogen the structure was always partly destroyed and no certain observations could be made. But when we come to unchanged cellulose, we find this decidedly and strongly flashing up yellow to orange, and here and there with rainbow colors. As the effects of polarization are produced not merely by the chemical composition, but also by the physical structure of the fibers, it is out of the ques- to make such sharp distinctions as stated by some of the previous observers. All we can say is, we can *with certainty* distinguish firstly, any *unchanged cellulose* by its very strong flashing up in yellow, orange, and variegated (rainbow) colors; secondly, highly nitrated products (from 12.75 per cent. nitrogen upwards) by flashing up not so strongly in blue colors. Further distinctions are *not* possible, even in the case of high degrees of nitration. When working for collodion cotton, where the structure of the fiber is to some extent affected, and there is more unchanged cellulose present, the polarization microscope renders no practical service. In the presence of only 5 per cent. unchanged cellulose a great part of the microscopic field appears yellow, and with 15 per cent. cellulose the phenomena of polarization of the nitrated fibers are entirely obscured. Hence the polarization is a useful means for qualitatively detecting the presence of small quantities of unchanged cellulose in highly nitrated products, but it fails in the case of collodion cottons.

E. Behavior of Nitrocellulose towards Iodine.—According to Guttmann,[1] Kindt states that when treating nitrated cellulose with a solution of iodine in potassium iodide, and subsequently moistening with dilute sulphuric acid, guncotton becomes yellow, while cotton turns blue. We found when following this direction, that the yellow or brown color does not proceed from any action of iodine upon the nitrated fiber, for it is entirely removed by washing. When treating with iodine solution alone, without sulphuric acid, and subsequently washing with water, the most highly nitrated products (guncotton proper) lost their color; the less strongly nitrated products retained a brown color increasing with the *decrease* of nitration, but not at all with sufficient regularity to base any clear distinction thereon. In all probability, this phenomenon is caused by the formation of oxycellulose, of which several modifications are known to exist.[2] At any rate, the above-mentioned reagent did not prove of any value.

F. Quantitative Estimation of Unchanged Cellulose in Nitrocelluloses.—During the progress of our work, the necessity frequently arose for quantitatively estimating any admixture of unchanged cellulose in the nitrated products. The methods described up to that time were thoroughly tested, but yielded quite unsatisfactory results. The oldest of these is based on a treatment with a hot concentrated solution of sodium sulphide; this is a very slow process and we never succeeded in obtaining a residue free from nitrogen. Hess and Schwab, and later on Eder, decomposed collodion cotton dissolved in ether-alcohol by an alcoholic solution of potash or soda, and this is also applicable to guncotton when dissolving this in acetone, but it is not easily carried through because the solution of sodium hydroxide in almost anhydrous alcohol takes place with great slowness, while the presence of a little more water militates against the reaction.

The following new process was found to answer the purpose in the case of the mere highly nitrated products. The reagent employed is an alcoholic solution of sodium ethylate (sodium methylate or amylate have the same effect), C_2H_5ONa, prepared

---

[1] *Loc. cit.*, **2**, 59.

[2] Compare Section III, *F.*

by dissolving 2 or 3 grams metallic sodium in 100 cc. 95 per cent. alcohol, which takes only a few minutes. The solution is filtered and is mixed with 100 cc. acetone. This reagent has no effect whatever on real cellulose, even after an action of several hours' duration, but nitrocellulose is almost instantaneously decomposed with formation of a reddish brown substance soluble in water, evidently the sodium salt of an organic acid, possibly connected with Will's oxypyruvic acid.[1] The operation is carried out as follows:

150 cc. of the 200 cc. prepared above are placed in a capsule or Erlenmeyer flask along with 5 grams of guncotton. The mixture is heated to 40° or 50° on a water-bath, and now and then shaken up during twenty or thirty minutes; or else it is allowed to stand at the ordinary temperature for a few hours. It is then allowed to settle. The brown-red solution is decanted from the undissolved portion; the latter is first washed with alcohol by decantation, and subsequently with water, whereby the brown substance is dissolved. The residue, consisting of cellulose, is filtered and washed with hot water, last of all with addition of a little hydrochloric acid. For ordinary work, it may be at once dried and weighed; for very exact estimations the water is removed by washing with alcohol, the residue is once more treated with 50 cc. of the reagent left over from the first treatment by keeping at 40° or 50° for fifteen minutes, and the operation is finished as above. The cellulose thus obtained does not yield a trace of gas in the nitrometer and gives only an extremely faint blue reaction with diphenylamine. It shows a very faint yellow color, produced by about 0.1 mg. of the brown substance which can be removed by treating with a solution of 0.1 mg. chloride of lime in 5 cc. very dilute hydrochloric acid; but this last treatment is really unnecessary, as the 0.1 mg. does not appreciably affect the estimation. The results agree to 0.1 or 0.2 per cent., if the weight of unchanged cellulose amounts to about 0.2 gram, which can be attained by employing a convenient weight of guncotton.

Guncotton entirely soluble in acetone contains only traces of cellulose. In the presence of 0.85 per cent. cellulose, the solubility is impaired; some fibers remain floating in the liquid. When 5 or 10 per cent. cellulose is present, a great part of the nitrocellulose does not dissolve in acetone.

---

[1] *Ber. d. chem. Ges.*, **24**, 400.

The described reagent, sodium ethylate, is applicable to the estimation of cellulose in guncotton and collodion cotton, but not in the products with lower nitrogen percentages which have as yet no technical application, but were prepared by us in order to study the various degrees of nitration (Section III, *C*). In the case of these products, which always contain much unchanged cotton fiber, the sodium ethylate method yields results, varying by 5 or even 10 per cent. and is, therefore, quite useless. The reason for this is no doubt the fact that these products, which are prepared with less highly concentrated acids, always contain *oxycellulose.* Since this substance is soluble in alkaline liquids, the percentage found by alkaline reagents of nitrocellulose appears too high. We shall treat of the formation of oxycellulose in a subsequent section (III, *F*).

III. METHODS FOR OBTAINING THE VARIOUS NITROCELLULOSES.

The first chemists who worked on nitrocelluloses adopted for cellulose the formula $C_6H_{10}O_5$, and consequently spoke of "trinitrocellulose," $C_6H_7(NO_2)_3O_5$, as the highest obtainable term, while "dinitrocellulose," $C_5H_3(NO_2)_2O_5$, was supposed to represent the composition of "soluble" nitrocellulose. The former expression is still sometimes used to denote guncotton (pyroxylin), the latter for denoting collodion cotton.

Of course it has been known for a long time past that the molecule of cellulose must be a multiple of $C_6H_{10}O_5$, but its real magnitude is not known and is not of much importance in this connection. All we need is to fix the lowest figure by which we can represent the various products obtainable by introducing NO_2 groups (nitric acid radicals) into the molecule of cellulose.

Eder[1] obtained four degrees of nitration from the highest downwards, and consequently doubled the ancient formula, as he required the molecule $C_{12}H_{20}O_{10}$ to represent all his products. Vieille,[2] however, obtained within the same limits a greater number of distinct products and found himself compelled to use the molecular formula $C_{24}H_{40}O_{20}$ for cellulose. This would cause the highest degree of nitration to be called "dodecanitrocellulose," in lieu of the old term "trinitrocellulose" or Eder's "hexanitrocellulose," but Vieille could not obtain this highest term at all and declared "endecanitrocellulose," $C_{24}H_{29}(NO_2)_{11}O_{20}$, to be the highest prod-

[1] *Ber. d. chem. Ges.*, **13**, 169.

[2] *Compt. rend.*, **95**, 132.

uct of nitration obtainable. The table given in Section II, *A*, gives the formulas and nitrogen percentages of the various stages of nitration denoted according to the $C_{24}\cdots$ molecule, which we adopt throughout this paper as being sufficient for representing our present stage of knowledge.

Mendelejeff[1] obtained a product containing 12.44 per cent. nitrogen entirely soluble in ether-alcohol, whose nitrogen percentage is about midway between Vieille's deca- and enneanitrocellulose. Vieille had stated that deca- was insoluble, ennea- soluble, and therefore Mendelejeff considered his soluble intermediate product as a new, individual step of nitration which would compel the adoption of a formula containing C_{48}. But as we shall see later on, there exists a soluble decanitrocellulose, and there is hence no reason whatever for making the solubility of Mendelejeff's products a criterion of its nature as an individual compound ; it may very well have been a mechanical mixture of the deca- and ennea-body. I do not, therefore, at present see any reason why we should write our formulas on the basis of $C_{48}\cdots$, and I shall retain the basis of $C_{24}\cdots$ by which all our results can be satisfactorily expressed. Of course the real formula must be $nC_{24}\cdots$, but we may neglect the unknown value of n as immaterial for our purposes.

The lower members of the series of nitrated celluloses, up to deca-, can be obtained by means of nitric acid alone, but as even these in actual practice are always prepared by mixtures of sulphuric and nitric acids, we have almost exclusively worked with such, and we shall now proceed to discuss the conditions for obtaining the various steps of nitration.

A. On the Highest Stage of Nitration Obtainable from Cellulose.

As the older work on this subject may be considered obsolete, especially in view of the improvement of the methods for estimating the nitrogen, we may begin with the statement of Eder.[2] The most highly nitrated product he obtained was made by the action on cellulose of a mixture of three parts concentrated sulphuric acid and one part fuming nitric acid, and treating the product with ether-alcohol by which from 1.2 to 5.8 per cent. of soluble substances were extracted. He thus obtained a substance showing by analysis the following percentages of nitrogen: 13.91,

---

[1] *Moniteur Scientifique*, 1897, p. 510.

[2] *Ber. d. chem. Ges.*, **13**, 176.

13.74, 13.82; and this he considered near enough to the percentage of 14.16, required for "hexa-" (C_{12} .. equal to our "dodeca-") nitrocellulose, to declare it to be essentially composed of this compound.

Vieille,[1] however, obtained under the same conditions a product showing only 214 cc. NO = 13.42 per cent. nitrogen, or very nearly 13.50, the percentage for endecanitrocellulose.

Vignon[2] attained only 213 cc. NO = 13.35 per cent. nitrogen again leading to endecanitrocellulose.

In the first series of experiments (with Weintraub) we treated each time 2.5 grams cellulose with 30 grams nitric acid (sp. gr. 1.52) and 90 grams sulphuric acid (sp. gr. 1.84) at a constant temperature of 15° during twenty-four hours; three different samples made in this way showed 13.37, 13.40, and 13.36 per cent. nitrogen. Another time, when treating the same mixtures at a temperature of 10° during ten hours, we obtained 13.39 per cent. nitrogen. That a change of temperature up to 40° or down to 0° does not produce higher nitrogen percentages, we shall see later on (Sec. III, *D*).

When increasing the quantity of sulphuric acid, the nitrogen percentage of the product is lowered; when decreasing it, it is decidedly, but slightly, raised as we shall see. The maximum thus obtained in this first series was 13.456 per cent. nitrogen, thus confirming Vieille's and Vignon's conclusion, that the action of a mixture of sulphuric and nitric acids leads only up to endecanitrocellulose. But their further conclusion, that no higher degree of nitration exists at all, could not be confirmed, for on applying mixtures similar to Hoitsema's[3] (*viz.*, equal parts of nitrogen pentoxide and phosphorus pentoxide), we obtained up to 13.88 and 13.90, sufficiently near to the percentage for dodecanitrocellulose and far above that for endecanitrocellulose.

The existence of dodecanitrocellulose has thus been confirmed both by Hoitsema and by ourselves, but it has been obtained only by the use of extraordinary reagents, not applicable in manufac-

---

[1] *Compt. rend.*, **95**, 132.

[2] *Ibid.*, June 6, 1898.

[3] *Ztschr. angew. Chem.*, 1898, p. 173.

[4] H. N. Warren, *Chem. News*, **74**, 239 (1896), claims to have obtained a "tetranitrocellulose" (C_6....), without quoting any analysis. Since he claims to have obtained this product by treating "trinitrocellulose" (guncotton) with a mixture of "equal parts by weight of commercial vitriol and phosphoric anhydride," which must have saponified and dissolved the guncotton and since he has not followed up his preliminary notice by communicating any details, we cannot treat his work seriously, any more than Hoitsema does.

turing practice. In my later experiments (with Bebie) we were more fortunate; we succeeded in getting up to the highest percentages of nitrogen by mixtures of sulphuric and nitric acids, as shown by the following table:

	Composition of acid mixture.			Nitrogen in product.	Yield on cotton.
No.	H_2SO_4.	HNO_3.	H_2O.	Per cent.	Per cent.
1	60.00	27.43	12.57	13.62	173
2	62.10	25.79	12.11	13.75	174
3	62.95	24.95	12.10	13.83	175
4	63.72	25.31	10.97	13.75	175
5	64.56	24.65	10.79	13.71	175

As this work had led to the very striking result that nitrogen percentages had been reached *exceeding anything previously obtained by the direct action of the mixture of sulphuric and nitric acids without extracting the products by ether-alcohol, and* that with mixtures *containing a comparatively large quantity of water*, I thought it advisable to test this result by a new series of experiments which turned out as follows:

	Composition of acid mixture.			Nitrogen in product.	Yield on cotton.
No.	H_2SO_4.	HNO_3.	H_2O.	Per cent.	Per cent.
6	68.02	25.28	5.70	13.76	...
7	64.55	26.55	8.88	13.72	173
8	63.35	25.31	11.34	13.92	173

Here, with 11.34 per cent. water in the acid mixture, we obtained 13.92 per cent. nitrogen[1] *quite as high as Hoitsema and ourselves with the phosphorus pentoxide mixture*, that is, close to the composition of perfectly pure dodecanitrocellulose (= 14.16 per cent. nitrogen).

We shall later on discuss the influence of varying quantities of water on the process of nitration; in this place I wished only to prove the existence of dodecanitrocellulose. I must, however, add that this product, as obtained by us, is not a *stable* compound. The sample giving 13.92 per cent. nitrogen was preserved under water for a few months and then dried and tested again; it now showed only 13.5 per cent. nitrogen. On repeating the experiments we at once obtained products up to 13.8 per cent. nitrogen but usually only the first tests yielded these values; after a few days' standing in the desiccator the percentage was only 13.5 per cent. and remained perfectly constant at this point, equal to

---

[1] It may be said, once for all, that there is no question of experimental errors in our analyses. Every one of our nitrogen estimations was *at least made in duplicate*, the discrepancies generally ranging within 0.01, very rarely up to 0.015 or 0.02 per cent. nitrogen.

endecanitrocellulose. The latter therefore appears to be the highest *stable* degree of nitration.

To prevent any suspicion that those extraordinarily high nitrogen percentages might be due to some nitric acid being retained in the product, every precaution was taken in washing the latter, and special check tests proved that the above could not possibly have been the case.

Special experiments were made with a view of ascertaining whether by avoiding the use of hot water in washing the products, the nitrogen percentage could be raised, but this course did not lead to more than 13.53 per cent. nitrogen and the product in question, although treated with sodium carbonate, exploded at 150° which proves it to be too unstable for any practical use.

Some further experiments showed that the proportion of sulphuric to nitric acid which, in the experiments 1 to 8, had been about 2.5 : 1, may be varied up to 3.3 : 1 and down to 2 : 1 without making a difference in the result.

	Composition of acid mixture.			Nitrogen in nitrocellulose.	Yield.
No.	H_2SO_4.	HNO_3.	H_2O.	Per cent.	Per cent.
9	75.33	22.80	1.87	13.53	176
10	74.16	22.12	3.72	13.51	175
11	72.97	21.63	5.40	13.57	...
12	69.90	20.45	9.65	13.64	177
13	68.31	20.49	11.20	13.61	176
14	67.43	19.37	13.20	13.25	172
15	67.32	32.53	0.15	13.62	176.5
16	65.41	31.34	3.25	13.57	175
17	63.75	30.80	5.45	13.63	176
18	70.68	29.31	10.01	13.68	176

Those experiments further prove *that by lowering the proportion of water to a minimum* (which was effected by addition of fuming oil of vitriol), *the percentage of nitrogen in the product was not raised, and that it is, therefore, quite useless to make the process more expensive by employing such highly concentrated acid mixtures.*

B. Various Conditions to be Observed in the Nitrating Process.

The primary object of this investigation was that of establishing the conditions for obtaining with certainty the various descriptions of nitrocellulose required in commerce, from the most highly nitrated guncotton down to collodion cotton, but over and above that to somewhat exhaustively study the process in its various bearings.

Evidently the greatest part is played in this respect by the dilution of the nitrating mixture. This may be stated in the first instance in terms of the percentage of *water* present; but the *proportion of sulphuric to nitric* acid must also be taken into consideration, as well as the temperature and the *time* occupied by the process. Lastly, it must be ascertained what part is played by that unavoidable impurity present in nitric acid, *viz.*, the *lower oxides of nitrogen.*

In order to attain my ultimate object it was necessary to investigate all these various conditions apart from one another, that is, varying only one of them at a time, while keeping the others as nearly uniform as the case would permit. Unless this is observed, a thorough solution of the task cannot be expected. My predecessors, with all their eminence in the field of explosives, have nothing like sufficiently fulfilled the condition just laid down. Thus Vieille[1] nitrated cotton with twelve different mixtures of sulphuric acid (sp. gr. 1.832) and nitric acid (sp. gr. 1.316) and obtained nitrocelluloses varying from 8.32 to 12.28 per cent. nitrogen. But in these experiments there were *two* variable magnitudes (namely HNO_3 and H_2O), and the results must depend upon both jointly. The same must be said of the numerous experiments made by Bruley.[2] To avold this drawback in our case, certainly much labor was involved ; several hundreds of nitrations, all followed up by careful analysis and other tests, and four years' work were expended upon this task which we shall now proceed to describe.

C. *Influence of Water on the Nitrating Process.*

In this series of experiments the proportion of sulphuric and nitric acids was kept practically constant, *viz.*, as nearly as possible equal (nitric acid slightly prevailing), and only the proportion of *water* was varied. The mixtures were prepared from "chemically pure" sulphuric acid (sp. gr. 1.83) and pure nitric acid (sp. gr. 1.50), which had been carefully freed from lower nitrogen oxides. The amount of water was varied by adding pure water, or, for the highest concentrations, by adding free sulphur trioxide in the shape of fuming sulphuric acid. The other factors, temperature,

---

[1] *Mem. des poudres et salpêtres*, **2**, 217.

[2] *Ibid.*, **8**, 111.

duration of action, proportion of cellulose to the acid mixture, were kept as constant as possible. The temperature was kept between 16° and 18°; the duration of action was twenty-four hours. The kind of cellulose used and the apparatus employed have been described in Section I, as well as the method of washing, drying, etc. Each experiment was (as during the whole of this work) made at least twice over, as well as the analysis of each of the products obtained, but as there was in every case a good concordance of results, I quote only the mean result of each separate variation of proportions.

The analytical methods employed are described in Section II.

They extended to the nitrogen percentage, the solubility in ether-alcohol (3 ether, 1 alcohol), the yield and the behavior in polarized light.

The results of the first series of nitrations are as follows :

				Acid mixture in per cent.		
No.	Nitrogen. Per cent.	Soluble in ether-alcohol. Per cent.	Yield cotton. Per cent.	H_2SO_4.	HNO_3.	H_2O.
1	13.65	1.50	177.5	45.31	49.07	5.62
2	13.21	5.40	176.2	42.61	46.01	11.38
3	12.76	22.00	....	41.03	44.45	14.52
4	12.58	60.00	167 0	40.66	43.85	15.49
5	12.31	99.14	159.0	40.14	43.25	16.61
6	12.05	99.84	153.0	39.45	42.73	17.82
7	11.59	100.02	156.5	38.95	42.15	18.90
8	10.93	99.82	144.2	38.43	41.31	20.26
9	9.76	74.22	146.0	37.20	40.30	22.50
10	9.31	1.15	138.9	36.72	39.78	23.50
11	8.40	0.61	131.2	35.87	38.83	25.30
12	6.50	1.73	....	34.41	37.17	28,42

These results have been plotted on the accompanying diagram, the upright lines showing on one side the number of cubic centimeters of NO evolved per gram of the product, on the other side the nitrogen percentage of the same, and the horizontal lines showing the percentage of water in the acid mixture. It appears that the single results (marked by circlets) arrange themselves in a very regular curve which allows of foreseeing the nitrogen percentage of the product for the varying proportions of water in the acid mixtures employed for nitration.

As might be expected, and as is especially shown by a glance at the third column of the preceding table (the solubility in ether-alcohol), the products obtained mostly, were not chemically pure individual compounds, but mixtures of various stages of nitration.

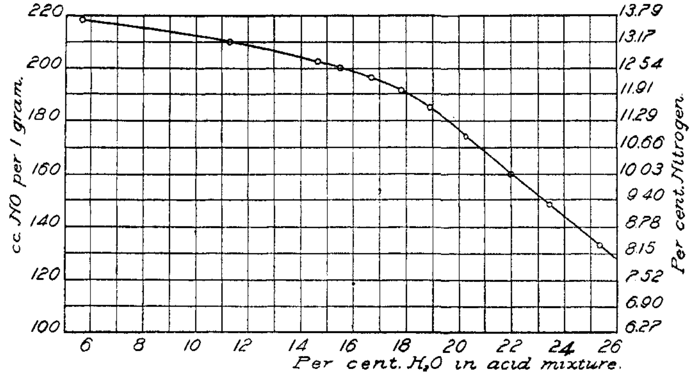

Diagram 1.

The solubility in ether-alcohol may be made use of for at least a partial separation of the products of nitration. Of course, both the soluble and insoluble portions might be assumed to consist of a mixture of various nitrocelluloses, but frequently their nitrogen percentage shows them to be of uniform nature. Where either the soluble or the insoluble portion amounted but to a few per cent. of the whole, lack of material precluded their separate investigation, and in these cases, only the prevailing portion was separately analyzed and the nitrogen percentage of the portion indirectly estimated by the following mode of calculation.

Suppose we have directly estimated the nitrogen percentage of the insoluble portion, *a* denoting the nitrogen percentage of the entire mixture obtained by nitration and *c* the percentage solubility in ether-alcohol. We shall learn the nitrogen percentage *d* of the soluble portion by the formula

$$d = \frac{100\ (a-b) + b.c}{c}.$$

If, on the other hand, the nitrogen percentage *d* of the soluble portion is known, we learn the percentage *b* of the insoluble by the formula

$$b = \frac{100\ a - d\,c}{10-c}.$$

Considering that the estimation of solubility is not a very accurate operation, especially in the case of low solubilities, we cannot ascribe a very high degree of accuracy to these indirect estimations of the nitrogen percentage, but they will, at all events, sufficiently elucidate the progress of nitration.

We shall now discuss the single results a little in detail. No. 1 shows a product of strikingly high nitrogen percentage, exceeding the highest attained by Vieille. This product was obtained with an acid mixture containing 5.62 per cent. water; we have seen in Section III, *A*, that even higher percentages of nitrogen can be obtained with mixtures containing rather more water, but also more sulphuric acid than was employed in this case. The nitrogen percentage increased but very little by extraction with ether-alcohol, *viz.*, to 13.67, that of the soluble portion being calculated as 12.54 per cent.

An increase of the percentage of water to about 11 per cent. caused a slight diminution of the nitrogen percentage. In Section III, *A*, we have seen that with the same percentage of water, but with more sulphuric acid, the maximum percentage of nitrogen was attained. The insoluble portion of No. 2 contains 13.37 per cent. nitrogen and is, therefore, practically equal to endecanitrocellulose. The soluble portion is calculated to contain 11.35 per cent. nitrogen.

The nitrogen percentage of No. 3 (12.76) is exactly like that of decanitrocellulose (theoretically 12.78); but its partial solubility shows that it was not a chemical individual, and its nitrogen content only accidentally agreed so well with decanitrocellulose (Eder's pentanitrocellulose). It could be split up into 22 per cent. of octonitrocellulose, with 11.10 per cent. nitrogen (theory 11.13) and 78 per cent. of another substance, showing by calculation as above 13.23 and by actual analysis 13.26 per cent. nitrogen. This is a strong warning against drawing conclusions on the solubility and other properties of technical nitrocellulose from its accidental percentage of nitrogen, which subject we shall have to mention again further on.

The difference between the degree of nitration of the soluble and insoluble components of the samples hitherto discussed is no doubt caused by the dilution of the acid mixture taking place during the nitrating process, firstly by the positive formation of water, secondly by the abstraction of nitric acid. Since these experiments show that a difference of a few per cent. of water may produce greatly differing stages of nitration, we understand why, during the nitrating process, where there is a chemical production of free water, various nitrocelluloses must be produced. The variations must be less prominent, the greater the proportion of acids to that of the cotton, and the lesser consequently the absolute changes in the composition of the acid mixture. This explains why the proportion between the quantity of cotton and that of the acid mixture is an important factor in the process.

Combining the knowledge to be derived from the experiments hitherto discussed (made with about equal quantities of sulphuric and nitric acids and water up to 11 per cent.) with those described in the preceding section (where the ordinary mixture of 3 sulphuric to 1 nitric acid was applied with varying quantities of water), we arrive at the conclusion that *in order to make guncotton of a high percentage of nitrogen it is quite unnecessary to employ acid mixtures containing only a few per cent. of water.* With the acid proportion 1 : 1 it is permissible to go up to 10 per cent. water, with 3 sulphuric to 1 nitric acid even *up to 12 per cent. water*, and *consequently to work with much cheaper acids than is usually done.*

From Professor Will's paper on the stability of nitrocellulose which I have received at the last moment before closing this paper, and which will be referred to later, I notice that under otherwise equal conditions and equal relation between sulphuric and nitric acid, *the rapidity with which nitrogen is given off from the nitrocellulose at a temperature of 135°* (which he considers to be the surest test for the stability of nitrocelluloses) *decreases with the increased percentage of water in the nitrating acid.* The same amount of decomposition as is brought about in fifty-five minutes with a mixture containing 4 per cent. water, required 255 minutes with a mixture containing 9 per cent. water. *This greatly increased stability is another strong argument for the recommendation which I have derived from my experiments, to employ acid mixtures containing more water than has been hitherto the custom.*

No. 4 of the above series is an intermediate mixture; with No. 5 we reach the series of completely soluble products, that is, the *collodion cottons.* As the curve shows, the influence of the increase of water now becomes much stronger. Over 18 per cent. water the nitrogen percentage quickly decreases with the increase of water. The group of entirely soluble nitrocelluloses, with from 12.31 to 10.93 per cent. nitrogen, is obtained by acid mixtures ranging between 16.6 and 20.3 per cent. water. Between

Nos. 7 and 8 we should find the typical collodion cotton, *viz.*, octonitrocellulose, with 11.13 per cent. nitrogen, and by interpolation on the curve we find the corresponding amount of water in the acid mixture = 19.5 per cent. This conclusion was confirmed by actual experiment. An acid mixture containing the same proportions of sulphuric and nitric acids as employed above, and 19.42 per cent. water, yielded *practically pure octonitrocellulose, and we have thus shown how to obtain with all certainty this product* which is of such great technical importance, and which is usually assumed to be somewhat difficult to manufacture with regularity.

I must here interpose some remarks on a paper published by Wyss-Naef[1] upon the preparation of collodion cotton, to be employed in the manufacture of vegetable silks at the Besançon factory. According to him this collodion cotton is made by treating cotton during four to six hours with a mixture of 85 parts sulphuric and 15 parts fuming nitric acid (sp. gr. 1.52). He does not expressly speak of the concentration of the sulphuric acid, but he must evidently mean the ordinary concentrated oil of vitriol (66° Baumé), for he speaks of the strong attraction of the acid mixture for water, and moreover nobody would for a technical process employ such costly nitric acid as that of 1.52 specific gravity, to mix with dilute sulphuric acid, instead of the much cheaper mixture of concentrated sulphuric and weaker nitric acid.

Wyss-Naef's statements have been reproduced without criticism in a recently published book by Dr. Süvern, "Die künstliche Seide."

It would have been an extremely valuable service to the industry of collodion cotton if the detailed descriptions of Wyss-Naef on the process employed at Besançon could be accepted as correct, although it would be an almost unexampled instance of generosity on the part of the owners and managers of that factory to make such a present of their hitherto secret process to their competitors in trade. Unfortunately this is not the case. In the first paper published in 1899 by Weintraub and myself we had already shown that when carefully following the instructions of Wyss-Naef even after three days some raw cellulose was left behind, that the final product contained 12.74 per cent. nitrogen, that it differed entirely from the published description in its

---

[1] *Ztschr. angew. Chem.*, 1899, p. 469.

behavior under the polarization microscope, and *that it contained only 19 per cent. of matter soluble in ether-alcohol.* Then we publicly challenged Mr. Wyss-Naef to clear up these contradictions, but received no answer.

Looking at the importance of this matter, I repeated with Bebie the operation as prescribed by Wyss-Naef, this time at slightly raised temperatures, as we had learned that such are employed at the factories of vegetable silk. The following figures show that by this, only some time was saved, as a matter of course, but that the products are just as little "soluble" nitrocellulose as in our former experiments.

Temperature.	Duration of nitration. Hours.	Nitrogen. Per cent.	Solubility Per cent.	Yield Per cent.
30°	4	12.53	17.14	160.2
40°	7	13.12	15.54	143.1

There was no unchanged cotton left behind. In the polarized light the fibers showed a faint steel-blue color.

I must, therefore, assume until further explanations, that the prescriptions of Wyss-Naef on the manufacture of collodion cotton are entirely untrustworthy, and I must adhere to the prescription given above from the experiments made in my own laboratory.

We now resume the discussion of these experiments. Below 10 per cent. nitrogen the solubility of nitriccellulose quickly decreases. The products from hexanitrocellulose downwards are insoluble, as previously found by Vieille. The soluble hexa- and tetranitrocelluloses, obtained by Eder with very hot acid mixtures, or by the action of alcoholic potash on more highly nitrated products are evidently of quite a different nature, since no cellulose could be regenerated by means of ferrous chloride, and they must be considered as not being nitrated celluloses at all, but nitric esters of other carbohydrates.

If the percentage of the acid mixture attains 25 per cent. or more, no complete nitration can be effected by an action of twenty-four hours; in No. 12, unchanged cotton was left, even after three days' action, to the amount of 4.1 per cent; the nitrated portion would then contain 6.78 per cent. nitrogen, and consists of tetranitrocellulose. But as mentioned in Section II, the estimation of the unchanged cellulose and consequently that of the nitrogen percentage in the other portion, can be only approximate in such cases.

In the presence of more water the nitration becomes less and less complete. In the beginning there is still some nitration, later on, only oxycellulose is formed, as shown by the entire or partial solubility in dilute alkali, precipitation from the solutions by acids or alcohol, intense coloration with basic coloring-matters, reduction of Fehling's solution and formation of compounds with phenylhydrazine.

The *morphological structure* of the products is strongly altered by an increase of water in the acid mixtures. Up to 15 per cent. water the original structure is preserved. At 18 per cent. water, the fibers appear somewhat contracted and the characteristic twist of cotton fiber is lost. With more water the fibers appear to be torn open and disaggregate into small particles which get felted into globular masses. This destructive action is at its maximum with 23 or 25 per cent. water ; by more dilute acid mixtures the fibrous structure is much less affected, but here also by prolonged action the fibers are split up into smaller elements.

A further series of tests was made to ascertain whether guncotton, made with acid mixtures containing from 8 to 11 per cent. water, as recommended by me in consequence of our investigations, might be *less resistant to boiling water* than those made with more concentrated acids. This did not seem very likely, but still it had to be examined.

For this purpose two nitrations were made simultaneously: (1) with the usual mixture (69.14 H_2SO_4, 23.91 HNO_3, 6.07 H_2O, 0.88 N_2O_4), and (2) with a mixture containing 63.64 H_2SO_4, 25.25 HNO_3, 10.82 H_2O. Both were treated exactly in the same way with cold, hot, and boiling water, and were tested for nitrogen percentage and explosiveness. The following were the results, *proving that guncotton made according to our prescription does not lose any more nitrogen on boiling with water than such made with more concentrated acids.*

		Product 1.		Product 2.	
No.	Kind of treatment.	Nitrogen. Per cent.	Explosion.	Nitrogen. Per cent.	Explosion.
1.	Washed one-half day cold, one day hot water	13.45	161° 3′9″	13.64	158° 3′5″
2.	Washed one-half day cold, three days hot	13.48	170° 4′40″	13.49	163° 4′30″
3.	Washed one-half day cold, one and one-half days hot, boiled two hours (no acid reaction in water)	13.47		13.50	
4.	The same boiled another five hours	13.36		13.45	

Product 2 behaves in the washing process exactly like 1; there is a trifling loss of nitrogen, which remains always slightly above 1, but this difference does not seem to be of any importance, no more than the slight difference in explosiveness.

Of course, only more extended experiments on the large scale could absolutely decide these questions, and the question of ballistic differences could not even be approached by us.

D. Influence of Temperature.

The experiments described in Section III, *C*, were all made at the ordinary temperature and lasted twenty-four hours. The question now arises how the process is affected by varying the temperature of the nitrating process. This was separately studied for the case of guncotton and that of collodion cotton.

For *guncotton* as nearly as possible 2.5 grams of cotton were nitrated with a mixture of 30 grams nitric acid (sp. gr. 1.52), and 90 grams sulphuric acid (sp. gr. 1.84). The duration of the process could not very well be raised above seven hours, as the temperature had to be watched throughout the process. The results are quoted in the following table. The "yields" refer to 100 parts of cotton employed; the "loss of cellulose" is calculated per cent. of cellulose employed from the formula: $100 - b(1 - 0.0201a)$, where b is the yield from 100 parts cellulose, and a the number of cubic centimeters of NO given off from 1 gram nitrocellulose.

Temperature.		Nitrogen. Per cent.	Yield. Per cent.	Loss of cellulose. Per cent.	No.
0°	½ hour	10.71	152.29	trace	1
	7 hours	13.19	173.29	trace	2
10°	7 hours	13.37	175.78	....	3
15°	7 hours	13.38	175.61	....	4
19°	½ hour	12.72	166.14	....	5
	7 hours	13.39	175.56	....	6
40°	½ hour	13.07	172.32	trace	7
	7 hours	13.06	169.62	1.61	8
60°	½ hour	13.08	169.18	1.95	9
	4½ hours	13.07	162.05	5.67	10
80°	¼ hour	13.07	161.23	6.52	11
	½ hour	13.12	125.17	27.45	12
	3 hours	13.12	81.52	52.76	13

From this the following conclusions may be drawn:

1. With the rise in temperature the speed of the process increases rapidly. At 0° the nitrogen percentage reached after half an hour is only 10.71, at 19° it is increased to 12.72, at 40° to 13.07 (which is the highest attainable at this temperature), and at 80° this is effected in a quarter of an hour.

2. *The nitrogen percentage of the product sinks a little when passing from ordinary temperatures (10° to 19°) to 40° (viz.,* from 13.39 to 13.06 per cent. nitrogen) *but remains practically at the same figure when nitrating at 60° or 80°.*

3. *The principal influence of the temperature of nitration is exerted upon the yield, which, when passing from the ordinary to higher temperatures, constantly falls.* This does not take place by direct solution of cellulose proper; first the cellulose itself is rapidly nitrated, and the nitrocellulose formed is thereupon partially dissolved, all the more quickly, the higher the temperature.

4. *By nitrating at higher temperatures the structure of the cellulose is changed.* It becomes short and fragile; that obtained at 60° or 80° is a finely fibrous powder after drying.

If the proportion of sulphuric to nitric acid is larger than the usual 3 : 1, the loss of yield and the solubility on raising the temperature of nitration are even more strongly pronounced. With 11 sulphuric to 1 nitric acid an increase by a few degrees of temperature has the same effect as 20° or 30° with the acid proportion 3 : 1.

It is also necessary for each temperature to find out the most suitable *duration of the action of the acids.* At the ordinary temperature there is a wide margin in that respect, but at higher temperatures we observe that the nitrogen percentage rises at first and on longer action decreases again. Thus the same acid mixture (3 : 1) at a temperature of 32° produced the following nitrogen percentages:

Time of action. Minutes.	Nitrogen. Per cent.
5	13.27
15	13.44
30	13.47
60	13.50
120	13.40

Hence the maximum was reached in this special case after an hour's action.

Looking at all circumstances, we conclude that in manufacturing guncotton the ordinary process of not exceeding a temperature of 25° during the nitration is right. We thus obtain a maximum percentage of nitrogen and a maximum yield within a reasonable time.

We now pass to *collodion cotton*, where a somewhat higher than the ordinary temperature is frequently employed in practice. Here the mixture of acids was employed which is mentioned in Section III, *C*, Experiment 7; *viz.*, 38.95 H_2SO_4, 42.15 HNO_3, 18.90 H_2O. The results were :

No.	Temperature.	Time of nitration. Hours.	Nitrogen. Per cent.	Solubility in ether-alcohol. Per cent.	Yield. Per cent.
14	17°	4	11.50	95.60	155.1
15	17°	24	11.59	99.81	156.2
16	40°	4	11.49	99.58	148.1
17	60°	1/4	11.46	99.71	146.7
18	60°	4	10.81	99.82	152.0

At 17° the *nitration* is practically completed in four hours; the yield is rather larger than at 40°, but the *solubility* was not quite so good, the product dissolving both more slowly and less completely.

At 40° the solubility is excellent, the yield decidedly less, and the nitrogen percentage is normal.

At 60° about the same result was accomplished after a quarter of an hour; after this the nitrogen percentage was lower. The structure of the cotton is to a great extent destroyed at this temperature. Although Experiment 4 showed that about as good a percentage and solubility can be attained at 60° in one-fourth hour, as at 40° in four hours, the change of structure seems to have ulterior consequences, for, as I am informed from reliable practical authority, the collodion cotton made at such high temperatures does not yield vegetable silk fit for spinning. Probably simultaneously with the change of morphological structure the cellulose molecule is also changed.

Our conclusion is that about 40° is the best temperature for obtaining collodion cotton, as this gives a maximum of solubility within a reasonable time (four hours), with no change of structure and comparatively little danger of overdoing the action.

E. Influence of Varying the Proportion of Sulphuric Acid to Nitric Acid.

The only observation I have found in the above respect is by Vieille[1] : "A great excess of sulphuric acid influences especially the speed of the reaction which is greatly lessened."

---

mpt. rend., 1895, p. 132.

The first series of experiments was made in cooperation with Weintraub. Each time 2.5 grams cotton were taken with 30 grams nitric acid (sp. gr. 1.52) and varying quantities of sulphuric acid ; only in the cases where very little or no sulphuric acid at all was employed the quantity of nitric acid had to be increased, in order to soak the cotton thoroughly well. The experiments were made at the ordinary temperature, which at that time was from 19° to 20° and was kept quite constant during the shorter experiments, but became somewhat lower during the nights, reaching 15° and even 13°. Section III, *D*, shows that this would have no perceptible influence on the results in the case of mixtures containing up to 3 sulphuric to 1 nitric acid. Special experiments, described in our German paper, show that the difference between 13° and 20° is perceptible when the proportion of sulphuric to nitric acid is 7 : 1 and more so when it is 11 : 1, but not to the extent of altering the conclusions to be drawn.

TABLE I.

		One-half hour.		Twenty-four hours.		Three days.	
Nitric acid.	Sulphuric acid.	Nitrogen. Per cent.	Yield. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Nitrogen. Per cent.	Yield. Per cent.
1	0	12.58	162.75	12.62	163.32	....	....
1	$\frac{1}{10}$	....	....	12.66	165.02	....	....
1	$\frac{1}{4}$	13.45	175.69	13.44	175.77	....	....
1	$\frac{1}{2}$	....	....	13.42	175.22	....	....
1	1	13.36	174.56	13.39	174.75	....	....
1	2	13.23	174.14	13.32	175.98	....	....
1	3	12.72	166.14	13.40	176.44	13.38	175.55
1	4	....	....	13.20	175.12	....	....
1	5	8.14	130.88 (25.44 unchanged cellulose.)	13.10	166.60	....	....

TABLE II.

		Three days.			Eight days.			Fifteen days.		
Nitric acid.	Sulphuric acid.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.	Nitrogen. Per cent.	Yield. Per cent.	Unchanged cellulose. Per cent.
1	6	12.63	162.40	0.85	....	....	....	12.74	169.80	none
1	7	10.86	151.60	10.46	....	....	....	....	....	....
								Thirty days.		
1	8	....	....	....	10.88	144.62	10.7	11.70	152.0	4.48
1	9	77.4	120.11	much	....	....	....	....	....	....
1	10	....	....	....	5.43	65.0	41.12	....	....	....

The conclusions arrived at from that series were as follows :

1. With the increase of the quantity of sulphuric acid the speed of the process decreases rapidly. Up to equal parts sulphuric and nitric acid the final stage of nitration is reached in half an hour. With acids in the proportion of 3 : 1 the first half hour brings us only to 12.72 per cent. nitrogen, the final stage being 13.40 per cent. nitrogen ; with 8 : 1 the final stage is not reached even after eight days, and only after thirty days is it equal to 11.70 per cent. nitrogen.

2. The maximum of nitrogen percentage of the products is obtained if the proportion of sulphuric to nitric acid is not less than 1/4 : 1, and not more than 3 : 1. Above 3 : 1 the nitrogen percentage falls first slowly, then more rapidly, but we must not overlook that with a very great excess of sulphuric acid a difference of a few degrees of temperature equally affects the result very seriously. (Compare the more detailed investigation of this point further on.)

3. Above a certain proportion of sulphuric to nitric acid (apparently 8 : 1) the final product always contains unchanged cellulose.

4. An excess of sulphuric acid affects also the structure of nitrocellulose. When employing pure nitric acid or up to 0.5 sulphuric to 1 nitric acid, the fibers contract and become more resisting. Beyond 7 : 1 the cellulose fibers are destroyed, and on drying fall into a finely fibrous powder.

These experiments had shown that with nitric acid alone the nitration cannot be driven beyond decanitrocellulose. *Collodion cotton*, consequently, might be prepared with nitric acid alone, but practically, this is never employed, since by the addition of sulphuric acid a great saving of nitric acid and of time is effected. There is not very much known about the best proportions of acids for preparing collodion cotton ; the published statements vary from 1 sulphuric to 1 nitric acid up to 6 : 1, and are partly decidedly misleading (compare above sub *C*). We have in Section III, *C*, shown the results obtained with that proportion of acids which is probably the best for collodion cotton ; *viz.*, about 1 : 1, with from 18 to 20 per cent. water in the mixture. I now give the results of experiments (with Bebie), intended to study more completely the conditions of making collodion cotton when varying the quantities of the acids and the proportions of water.

	Nitrating mixture.				Product.			Proportion of HNO_3 in acids to 1 cellulose.
No.	Parts H_2SO_4 to 1 part HNO_3.	H_2SO_4. Per cent.	HNO_3. Per cent.	H_2O. Per cent.	Nitrogen. Per cent.	Solubility in ether-alcohol. Per cent.	Yield. Per cent.	
1	3	62.18	21.91	15.91	13.21	3.20	174	30
2	3	61.53	20.02	18.45	12.42	98.70	160	30
3	3	60.30	19.71	19.99	11.72	99.28	157	30
4	3	58.88	19.60	21.52	10.96	99.50	148	30
5	3	59.77	20.94	19.29	11.74	99.98	159	12
6	3	58.34	20.62	21.04	10.90	99.20	149	12
7	3.8	63.84	16.96	19.20	12.08	....	163	30
8	3.8	62.52	16.46	21.02	11.23	....	153	30
9	3.8	63.84	16.96	19.20	11.76	....	156	12
10	3.8	62.52	16.46	21.02	10.99	....	151	12
11	5	67.60	13.66	18.74	12.43	....	167	30
12	5	66.37	13.04	20.59	11.66	....	148	30
13	5	64.85	14.90	20.25	10.53	....	140	8
14	5	64.11	13.62	22.27	9.35	....	...	8

No. 1, prepared with too little water, is still a guncotton. No. 2 is evidently identical with Mendelejeff's "pyrocollodion," both as to its nitrogen percentage and its solubility. The remaining samples are collodion cotton of various nitrogen percentages and various yields.

The differences between this series and the experiments described in Section III, *C*, where the proportion of acids was 1 : 1, is made very clear by the diagram appended here, in which the former series (with acids = 1 : 1) is represented by the dotted line; the full curve 1 shows the results obtained with sulphuric to nitric acid = 3 : 1; total acids = 30 to 1 cellulose; curve 2 refers to the same proportion, but 12 acids to 1 cellulose; curve 3 refers to

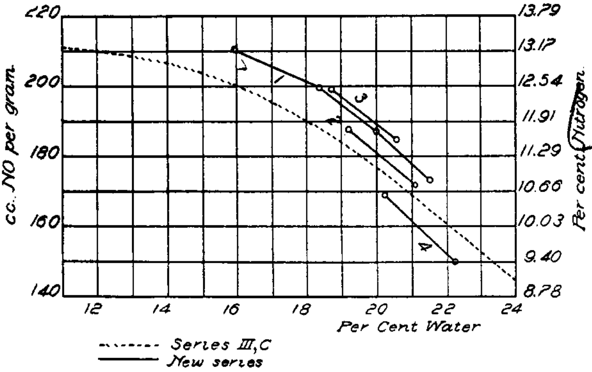

Diagram 2.

the acid proportion of 5 sulphuric to 1 nitric acid, and a total of 30 acids to 1 cellulose ; curve 4 refers to the same proportion of acids, but 8 total acids to 1 cellulose.

We see that the proportion of water being equal, an increase of the sulphuric acid from the proportion 1 : 1 to 3 : 1 causes an increase of 0.63 per cent. nitrogen in the product if the proportion of total acids is 30 to 1 cellulose, and an increase of about half as much, say 0.3 per cent. nitrogen, if the total acids are 12 : 1 cellulose. When increasing the proportion of water, the nitrogen percentage decreases quite as much with the acid proportion of 3 sulphuric to 1 nitric acid, as with 1 : 1.

The acid proportion 3.8 : 1 yields practically the same results as 3 : 1, and no curve has been drawn for this reason.

With the acid proportion 5 : 1 there was a very slight rise of nitrogen percentage in comparison with 3 : 1, but only if we employ 30 acids to 1 cellulose ; if this quantity is lowered to 8 acids to 1 cellulose, the nitrogen percentage of the product strongly decreases. In the former series of experiments there had been a slight *decrease* of nitrogen with this proportion of acids ; evidently there is not much difference either way.

All these experiments were made at the ordinary temperature and the nitration lasted twenty-four hours. Experiments made with the same acid proportions (1 : 3, 1 : 3.8, 1 : 5) at 35° showed that exactly the same results could be obtained at that temperature in two hours.

In the next following series of experiments, it was my aim to *keep the proportion of nitric acid to that of water perfectly constant and to vary only the sulphuric acid proper.* For that purpose, we started with nitric acid (sp. gr. 1.40) containing 184 parts HNO_3 to 100 parts H_2O, and added to this varying quantities of concentrated sulphuric acid, but as the latter contained 5.09 H_2O to 94.91 H_2SO_4, this 5 per cent. of water was always compensated by adding the calculated quantity of stronger nitric acid (sp. gr., 1.50), so that the proportion of HNO_3 to H_2O remained always as nearly as possible the same. Of course, the acid mixtures were always analyzed before use.

The experiments were made at the ordinary temperature and lasted 24 hours.

Up to 33 per cent. H_2SO_4, there was always unchanged cellulose left. On trying to estimate this it was found that the method described in Section II, *F*, did not yield very reliable results, owing to the formation of oxycellulose. I shall, therefore, not quote these experiments in detail, but describe only their general character.

Even nitric acid of 1.4 specific gravity by itself causes a partial nitration, but about 63 per cent. cellulose remained unchanged, no oxycellulose being formed here. The product, as a whole, contained 1.49 per cent. nitrogen, and the nitrated portion alone by calculation 4.00 per cent. nitrogen, which corresponds to *dinitrocellulose* (C_{24} . . .). As this product has never been obtained elsewhere, many attempts were made to isolate it by the action of solvents, or to prepare it otherwise in a purer state, but in vain.

By addition of 5 per cent. H_2SO_4 some oxycellulose was formed. The product contained about 58 per cent. unchanged cellulose, and 2.15 per cent. nitrogen; *trinitrocellulose* (C_{24} . . .) would contain 5.36 per cent. nitrogen. Here, as well, it was not found possible to isolate the products as a chemical individual.

I omit a description of the next experiments, with more sulphuric acid, where the mixture of nitrocellulose with oxycellulose and cellulose could not be properly unraveled, and I pass on to those where products free from unchanged cellulose were obtained, employing about 25 parts by weight of nitric acid and 14 parts water to 1 cellulose, the quantity of sulphuric acid being varied.

	Acid mixture.			Product.		
No.	H_2SO_4. Per cent.	HNO_3. Per cent.	H_2O. Per cent.	Nitrogen. Per cent.	Solubility. Per cent.	Yield. Per cent.
15	41.86	35.82	22.32	9.27	14.22	134
16	38.47	40.19	21.34	10.32	92.30	142
17	40.83	38.72	20.45	10.76	98.24	151
18	42.92	37.40	19.68	11.02	98.90	153
19	48.03	34.18	17.79	12.23	99.58	155
20	49.37	33.38	17.25	12.77	99.82	166
21	50.71	32.50	16.79	13.02	99.32	165
22	52.81	31.27	15.92	13.11	7.65	167
23	54.92	30.06	15.02	13.45	2.63	173

The product of No. 15 was treated by a solvent indicated to me by Dr. Brönnert as acting upon nitrocelluloses below octonitrocellulose; *viz.*, a solution of 4 parts calcium chloride in 100 parts alcohol of 95 per cent. This solvent extracted in the cold about 10 per cent., on boiling with reflux cooler another 35 per cent., but the remaining product contained almost exactly as much nitrogen as the raw product; *viz.*, 9.32 per cent. The portion insoluble in ether-alcohol is practically pure *hexanitrocellulose* (= 9.17 per cent. nitrogen).

Nos. 16, 17, 18, and 19 belong to the group of collodion cottons and call for no special remark. By a slight increase of sulphuric acid we get to a product. No. 20, having the exact composition of decanitrocellulose (theoretically 12.78 per cent. nitrogen), and still *completely soluble in ether-alcohol.* Even No. 21, with 13.02 per cent. nitrogen, is still completely soluble. This is a cogent proof that various forms of decanitrocellulose exist ; for both Vieille and myself (with Weintraub) had previously obtained *insoluble* decanitrocellulose (compare Section III, *G*). We then had worked with more concentrated acids; now, with more water, a *soluble* decanitrocellulose was obtained, which Eder had also prepared before.

Sir H. E. Roscoe, on the occasion of the "Cordite action," had also been able to make both soluble and insoluble nitrocellulose containing 12.8 per cent. nitrogen. H. C. Aspinwall[1] mentions that he obtained soluble nitrocellulose with 12.91 per cent. nitrogen.

These facts are of technical importance ; for in the manufacture of blasting gelatine and other blasting agents it is very important to employ *products soluble in ether-alcohol*, *with a maximum of nitrogen.* A discussion at a meeting of the New York Section of the Society of Chemical Industry[2] shows that the conditions for obtaining such products are not generally known, and probably they have been laid before the public for the first time by this present investigation.

By further increasing the quantity of sulphuric acid the solubility suddenly dropped to a minimum, with a very slight rise of nitrogen percentage. The last experiment, No. 23, led to practically pure *endecanitrocellulose*, that is the best guncotton obtained in ordinary manufacturing practice. This was done with a remarkably high dilution of 15 per cent. water in the acid mixture, while in practice much more concentrated acids are generally employed. It was just this circumstance which led us to further investigate the conditions for reaching the highest possible state of nitration, as described in Section III, *A*, where we have seen that these highly nitrated products were

---

[1] *Moniteur Scientifique*, 1900, p. 829.

[2] *J. Soc. Chem. Ind.*, 1900, p. 315.

reached with 11 to 12 per cent. water in the acid mixture, while mixtures with 6 down to 1½ per cent. water only led to endecanitrocellulose or little beyond.

Before closing this paper, I see from a paper by Professor Will just received, printed for private circulation, on the stability of nitrocelluloses (compare Section III, *C* and *G*) that under equal conditions. *an increase of the sulphuric acid in the acid mixture accelerates the decomposition of the nitrocellulose.* Up to 3 sulphuric to 1 nitric acid this acceleration is but slight, but it increases rapidly beyond that limit. This corroborates the conclusion at which I had arrived by my own experiments; *viz.*, that *for manufacturing guncotton of a high percentage of nitrogen it is advisable to work with a proportion of three parts sulphuric to one of nitric acid, but no more than this quantity of sulphuric acid.* Thus the maximum of nitrogen percentage and nearly the maximum of stability will be attained (*i. e.*, if the advice is followed given at the conclusion of Section III, *C*, concerning the proportion of water).

For the manufacture of *collodion cotton there is no reason for exceeding the proportion of equal parts of sulphuric and nitric acids, with from 19 to 20 per cent. water in the mixture.*

F. Formation of Oxycellulose in the Nitrating Process.

I have mentioned above that with more dilute acid mixtures oxycellulose is evidently formed, and probably nitrooxycellulose is present as well. Previously Brönnert[1] and Vignon[2] have noticed this, and they assert that also with concentrated acids oxycellulose is formed. This question seemed to require further elucidation.

Vignon founded his opinion on the observation that both nitrated cellulose and nitrated oxycellulose reduce Fehling's solution, and that this is independent of the degree of nitration. It is however a fact that other, probably more characteristic, reagents for oxycellulose do not act in the same way. The usual reaction for oxycellulose is its behavior towards basic coloring-matters, especially methylene blue, and this was applied to the case in question.

For each test 0.5 gram of the product to be examined was heated on the water-bath with 150 cc. of a 5 per mille solution of

---

[1] *Bulletin de Mulhouse*, 1900.

[2] *Compt. rend.*, September 10, 1900.

methylene blue during an hour, and, after cooling, 100 cc. were compared with 100 cc. of the original solution in a Lummer-Brodhuhn colorimeter in order to ascertain the loss of coloring-matter. The following results were obtained :

Nitrogen in nitrocellulose. Per cent.	Methylene blue, fixed by 1 gram. Gram.
0 (pure cellulose)	0.0012
13.65	0.0010
13.21	0.0009
12.76	0.0011
12.05	0.0021
10.93	0.0036
8.40	0.0120

This shows that the products obtained with concentrated acids contain no oxycellulose, but those obtained with dilute acids did contain such, and further tests confirmed this. The same result was obtained with Schiff's reagent for aldehydic groups (a solution of fuchsine decolorized by sulphuric acid).

G. Solubility of Nitrocelluloses in Ether-Alcohol.

I have had to refer on many previous occasions in this paper to the solubility of nitrocelluloses in ether-alcohol, by which we understand a mixture of 3 parts ether with 1 part alcohol. Here I quote in the first instance some experiments made specially with a view of deciding the behavior of decanitrocellulose in this regard.

By the action of nitric acid (sp. gr. 1.5) mixed with only 1/10 of its weight of sulphuric acid (sp. gr. 1.84), during twenty-four hours, a product was obtained containing 12.76 per cent. nitrogen ; that is, practically pure decanitrocellulose. This product was as good as insoluble in ether-alcohol to which it yielded only 2.1 to 2.25 per cent. The microscope showed a very uniform structure ; all fibers flashed up blue in polarized light. Hence, this product was most probably really an *insoluble* decanitrocellulose.

By nitrating as Vieille had done, with pure concentrated nitric acid, the same result was obtained.

When increasing the proportion of sulphuric to nitric acid over 3 : 1, the nitrogen percentage very slowly falls, but the *solubility in ether-alcohol rises.*

By the action of a mixture of 6 sulphuric to 1 nitric acid during fourteen days a product was obtained with 12.78 per cent. nitrogen, precisely like the percentage of decanitrocellulose, but it contained 19,17 per cent. soluble and 80.83 per cent. insoluble matter, the latter showing 13.08 per cent. nitrogen.

In our later experiments we obtained (Sec. III, *C*, No. 3) by the action of 41.03 per cent. sulphuric acid, 44.45 per cent. nitric acid, 14.52 per cent. water a product with 12.76 per cent. nitrogen of which 22 per cent. was soluble. I have pointed out before, that these results prove the product to have been mixtures of various degrees of nitration.

But in Section E, No. 20, we find a product with the exact percentage of decanitrocellulose, *completely soluble* in ether-alcohol (produced by the action of 49.37 per cent. sulphuric, 33.38 per cent. nitric acid, and 17.25 per cent. water).

All this, together with the results of Roscoe and of Aspinwall, proves that it is wrong to put the question in this way: "Is a nitrocellulose of 12.78 per cent. nitrogen, that is of the percentage of decanitrocellulose, soluble in ether-alcohol or not?" We have seen that by varying the proportions of acids and water in the nitrating mixture, quite a number of products may be obtained possessing the above nitrogen percentage, but varying in solubility from 0 to 100 per cent.; and evidently constituting quite different mixtures of such compounds.

A fortiori we cannot acknowledge as true decanitrocellulose the products obtained by Eder when treating for an hour and thus *dissolving* collodion cotton in nitric acid (sp. gr. 1.40) at 60°, which products contained 13.02 and 12.84 per cent. nitrogen and were easily soluble in ether-alcohol. By such energetic treatment as is produced by solution in hot nitric acid, the cellulose molecule must be thoroughly altered. When repeating Eder's experiments we obtained, by slightly changing the temperature, the time, and the quantity of acid, all sorts of products varying between 9.84 and 12.4 per cent. nitrogen; but we did not reach 12.78 per cent. The solution at first yields a precipitate with sodium carbonate; by longer digestion this property is lost. It then cannot contain either cotton cellulose or a nitric acid ester of this, as both would be precipitated by sodium carbonate. Evidently by the above treatment a variety of carbohydrates and their nitration products is formed, among which there may be some soluble compound of the percentage composition of decanitrocellulose, but quite different from the compound prepared in the usual way.

In this respect it is most interesting to note that it is possible to prepare *nitrocelluloses soluble in ordinary alcohol* (95 per cent.). When making the last-mentioned experiments (with pure nitric acid), we frequently got products containing 11 to 11.16 per cent. nitrogen which dissolved in alcohol with the greatest facility. This is the composition of *octonitrocellulose* (11.13 per cent. nitrogen), which according to Eder should be *insoluble* in alcohol ! These products are also soluble in concentrated nitric acid. Evidently they belong to a different class of compounds.

But it is even possible to obtain a compound of the composition of *decanitrocellulose*, which is *soluble in alcohol.* Hönig and Schubert[1] and Blondeau de Carolles[2] have described sulphuric acid esters of cellulose, soluble in water, which, when treated with alcohol, regenerate substances of the composition of cellulose, partly soluble, partly insoluble in water. When triturating cellulose with a small quantity of concentrated sulphuric acid in a glass mortar and adding to this a cold mixture of 3 parts concentrated sulphuric acid and 1 part concentrated nitric acid, we obtained nitrated products of snow-white color, soluble in alcohol, insoluble in ether and showing a nitrogen percentage varying with the temperature ruling during the action and the quantity of sulphuric acid. Even when trying to keep to the same conditions, the products varied from 10.22 to 11.29 per cent. nitrogen. By operating as follows we got up to much more highly nitrated products. About 2 grams of dry cellulose are completely dissolved in 50 cc. concentrated sulphuric acid and at once mixed with 25 or 30 cc. concentrated nitric acid, gradually run in from a drop funnel. The temperature should not rise over 15° which is secured by surrounding the vessel with ice. Now the mixture is allowed to stand at the ordinary temperature, which leads to the precipitation of a soft plastic mass. After twelve hours the whole is poured into a large quantity of water and this produces a precipitate of the following properties : It is a flocculent white powder, soluble in acetone, acetic ether, ethyl alcohol, methyl alcohol ; it is precipitated by water from the alcoholic solution as a gelatinous mass and can be purified in this

---

[1] *Monatsh. Chem.*, **6**, 708, and **7**, 455.

[2] *J. prakt. Chem.*, [2], **32**, 427.

manner. In concentrated nitric acid it dissolves with the greatest facility. Its nitrogen percentage is usually from 12.60 to 12.67, and it is therefore almost equal in nitrogen to decanitrocellulose; but occasionally we obtained as high as 13.80 per cent. nitrogen, and even this product was soluble in alcohol! We must probably look at these products as nitrated *cellulose-dextrines* or amyloids, and they must, of course, not be confounded with true nitrocelluloses.

Returning to the nitrocelluloses proper, as obtained in the usual way, we find that products soluble in ether-alcohol may be obtained almost down to the composition of heptanitrocellulose (10.19 per cent. nitrogen) and up to decanitrocellulose (12.78 per cent. nitrogen), or even beyond this. The collodion cotton of commerce, however, belongs more to the medium class of the composition of octonitrocellulose (11.13 per cent.) and enneanitrocellulose (11.98 per cent.). Where a high nitrogen percentage is not especially desired, but complete solubility is most important, it will be easiest to work for nitrogen percentages ranging from 11 to 11.5 per cent. by means of the acid mixtures indicated in Section III, *C*, Nos. 7 and 8, with nearly equal quantities of sulphuric and nitric acids, and from 19 to 20 per cent. water. These nitrocelluloses are insoluble in ordinary 95 per cent. alcohol, as well as in pure ether, but soluble in absolute alcohol. This might lead to the conclusion that in the ordinary ether-alcohol (3 : 1) the alcohol is the proper solvent. But this cannot be stated as a fact, for the solubility in absolute alcohol does not run parallel with that in ether-alcohol. The former rapidly decreases from 12 per cent. nitrogen upwards; at 12.04 per cent. nitrogen it is only 70 per cent.; the true decanitrocellulose which is perfectly soluble in ether-alcohol, yields only 1.3 per cent. to absolute alcohol.

A number of experiments were made to determine how far the mixture of ether (0.720) and alcohol (0.810) may be varied from the usual proportion 3 : 1. A nitrocellulose of 11.54 per cent. nitrogen dissolved easily in 6 ether to 1 alcohol; only 95 per cent. in 12 ether to 1 alcohol. In the last-mentioned case, 324 cc. ether to 26 cc. alcohol dissolved 1 gram nitrocellulose, which 26 cc. alcohol alone would not have done. A mixture of 27 ether to 1 alcohol dissolved only 7.3 per cent., on treating 1 gram with 350 cc.

In the other direction, 1/3 ether to 1 alcohol acted as a complete solvent; 1/6 ether to 1 alcohol dissolved only 93 per cent.;

but even with 1/5 ether to 1 alcohol the solubility was 95 per cent. This shows that the proportions of ether to alcohol may vary within very wide limits from the usual proportion of 3 : 1.

I append here the results obtained by examining various descriptions of *commercial collodion cotton*. This article, as everybody knows, is employed for extremely different purposes, and it seems likely from the outset that its properties, and hence, its composition and preparation should vary accordingly. For collodion cotton intended for surgical and photographic purposes, and for Chardonnet's vegetable silk, complete solubility in ether-alcohol is, no doubt, the most imperative requirement. When intended for blasting gelatine, that is, for forming a semisolid, tough mass with nitroglycerine, from 5 to 7 collodion cotton with 95 to 93 nitroglycerine, a high nitrogen percentage seems desirable together with solubility in nitroglycerine, which may not run parallel to that in ether-alcohol. Great secrecy is observed as to the manufacture of collodion cotton for both purposes, and even the composition of both is not sufficiently well known.

A sample of collodion cotton A, manufactured in Belgium expressly for blasting gelatine, showed 12.33 per cent. nitrogen and a solubility of 95.5 per cent. in ether-alcohol. Its explosion point, 198.5°, was almost exactly like that of collodion cotton B made for vegetable silk, 197°, and very little above that of guncotton. 13.25 per cent. nitrogen = 195°. The time of heating until explosion occurred, varied only from 4′ 4″ to 4′ 48″. The Abel test (Section III, *H*), in the case of guncotton occurred after 15′ to 17′ ; in that of collodion cotton B after 20′ to 24′. Cotton A did not give any result even after several hours, evidently owing to some admixture preventing the coloration of the test-paper.

We might infer from the above that collodion cotton, intended for the manufacture of blasting gelatine, should contain more nitrogen than that which is intended for dissolving in ether-alcohol. It should be prepared, according to our previous statement, with acid mixtures containing about 18.5 per cent. water.

I conclude this section with a few words on a paper by Kisniemsky[1] who has derived from Bruley's experiments a formula for calculating the nitrating mixtures leading to products of definite nitrogen percentages and definite solubilities. Taking

---

[1] *Mém. des poudres et salpêtres*, **10**, 64.

2 molecules HNO_3 as unity ($= 1$), and denoting 1 mol. H_2SO_4 by a, 1 mol. H_2O by c, he calls the magnitude $(1 + a) - c =$ the "characteristic" of the mixture. He asserts that mixtures with $\mu > 0$ yield products with much nitrogen and low solubility, mixtures with $\mu < 0$, soluble products, of which those where μ is only a like above $- 1$, contain the maximum of nitrogen.

It was not likely from the outset that the incomplete materials of which Kisniemsky disposed would lead to a mathematical formulation of the chemical action in question, an ambition which I do not even entertain for the much more complete materials offered in this paper. It may suffice to state that the indications yielded by his formula are quite uncertain and in many cases of the greatest importance they would be directly misleading. At all events they are useless for practical work.

H. Influence of the Lower Oxides of Nitrogen in the Acid Mixture on the Stability of the Nitrocelluloses.

Every description of commercial nitric acid, at least of higher strength, contains lower oxides of nitrogen. It is now generally assumed that in *concentrated* nitric acid (and we here deal only with such) the lower oxides consist essentially, if not exclusively, of nitrogen tetroxide, N_2O_4, formerly called "hyponitric acid," and generally considered as the mixed anhydride of nitrous and nitric acid, $NO—O—NO_2$. This view is, of course, greatly complicated by the fact that the vapor of nitrogen tetroxide begins to split up, when heated above its boiling-point, into molecules of NO_2, until at about 160° only such exist. But we need not go into a theoretical discussion of the behavior and constitution of this vapor, since we have here to deal merely with liquid N_2O_4, and this certainly behaves entirely as a mixed anhydride in presence of strong sulphuric acid, the reaction being $H_2SO_4 + N_2O_4 = NO_3H + SO_2(OH)(ONO)$; that is, nitrogen tetroxide then splits up into equal molecules of nitric acid and nitrososulphuric acid (chamber crystals).

Surely the above reaction is a reversible one, and therefore we must assume the presence of some N_2O_4 in any mixture of sulphuric acid, nitric acid, and nitrososulphuric acid; but the exhaustive investigation of this subject by Lunge and Weintraub[1] has shown that the amount of free N_2O_4 is extremely small, if

---

[1] *Ztschr. angew. Chem.*, 1899, pp. 393 and 417.

there are equal quantities of sulphuric and nitric acids present, and is reduced to mere traces where the sulphuric acid prevails.

Since in the manufacture of nitrocelluloses we have always to deal with a mixture of strong sulphuric and nitric acids, we must assume that any nitrogen tetroxide introduced by the latter is converted in the acid mixture half into nitric acid and half into nitrososulphuric acid. As nitrososulphuric acid is a derivative of nitrous acid and easily regenerates the latter in contact with water, alkalies, etc., it is *prima facie* not impossible that it might form nitrous esters with cellulose; and even mere traces of free N_2O_4 might lead to the same result, since, on being destroyed by esterification, they would be re-formed from the mixture of nitric and nitrososulphuric acids. Now the nitrous esters of cellulose might tend more to spontaneous decomposition than the nitric esters, and this would diminish the stability of nitrocellulose. All this, however, is entirely hypothetical, and only actual experiment can show whether the presence of N_2O_4 in the original nitric acid does or does not affect the properties of the guncotton manufactured from its mixture with sulphuric acid.

Berthelot[1], when saponifying nitroglycerine, found a considerable proportion of potassium nitrite along with nitrate. But even if we apply this observation to guncotton, which would be quite arbitrary, it affords no proof of the quantity of nitrous esters originally present (not formed by secondary reactions) and still less of their action concerning the stability of the guncotton.

Practical manufacturers mostly consider the presence of "low oxides" injurious in the manufacture of both nitroglycerine and guncotton.[2] But I can find no proof whatever for this opinion, except a paper of Payen's, from the earliest childhood of nitrocellulose.[3] He states that "hyponitric acid" diminishes both the yield and the nitrogen percentage of guncotton, and the guncotton thus produced also yielded inferior results with the ballistic pendulum, but there is nothing said about stability. Even if it were otherwise we could not acknowledge that ancient preparation of Payen's as a fair sample of guncotton and as a real proof for the action of N_2O_4.

Apart from the question of stability, I have found Payen's

---

[1] *Compt. rend.*, September 17, 1900.

[2] Compare, for instance, the discussion in the New York Section of the Society of Chemical Industry, *J. Soc. Chem. Ind.*, 1900, p. 645.

[3] *Compt. rend.*, **24**, 86, 1847.

assertion concerning the nitrogen percentage and yield to be erroneous. In 1898 we made comparative tests, adding to a mixture of 3 parts concentrated sulphuric and 1 part concentrated nitric acid, various quantities (*viz.*, 2.10, 6.43, 12.01 per cent. liquid nitrogen tetroxide) but with the first two mixtures we found exactly the same percentage and yield, and only when adding 12.01 per cent. N_2O_4, the nitrogen fell to 13.22 per cent., still quite a respectable figure. In 1900 we repeated this test, employing a mixture of 60.71 per cent. sulphuric acid, 30.67 per cent. nitric acid, 8.52 per cent. water, to which were added (as shown by analysis) various percentages of nitrogen tetroxide with the following results:

No.	N_2O_4 Per cent.	Nitrogen in guncotton. Per cent.	Yield. Per cent.
1	0.13	13.55	174.53
2	0.99	13.50	175.02
3	1.84	13.56	173.98
4	5.15	13.56	175.60

This proves that contrary to Payen's assertions and the opinion of many practical men *the presence of "low oxides" far above the proportion ever found in commercial acids has no influence whatever either on the nitrogen percentage or the yield of guncotton.*

This, of course, does not touch the question of stability. Before entering upon this, we had to ascertain which of the various methods for testing the stability of nitrocellulose was both trustworthy and applicable to our case. All these methods are empirical and to a great extent arbitrary, for they assume that the stability during a long period of ordinary (summer) temperatures, runs parallel with the evolution of nitrogen oxides during a short time of heating to higher temperatures. This may not, in reality, be the case, but I could not, of course, go behind the ordinary assumption, and it was merely the question of ascertaining which method it would be best to choose among those employed or proposed for testing commercial guncotton.

The oldest and even now most generally employed method is Abel's heat test, which is too well known to need description here. The principal objection to it is that it fails in the presence of mercuric chloride and perhaps of other substances added to commercial guncotton for the purpose of preventing mildew, but this of course could not interfere with our experiments, where no such ingredients come into play.

Principally on account of the just-mentioned drawback Guttmann proposed diphenylamine as an indicator. to be employed just like the potassium iodide in the Abel test, by observing a blue streak suddenly appearing between the wet and dry portion of the test paper.[1] Thomas[2] and Spica[3] reject Guttmann's test; but although we could certainly not notice the *sudden* appearance of the blue streak as described, we succeeded, after some practice, in obtaining sufficiently concordant results by means of that test as will appear below.

Spica himself recommends metaphenylenediamine which we had no opportunity of testing, as his communication reached me after the conclusion of that part of our work ; it is probable that this reagent would be *too* delicate for practical purposes.

Thomas indeed rejects all test papers as being too sensitive, and applies a pure heat test, consisting in heating the samples during eight or ten hours at 100° until red vapors appear.

A most interesting discussion on stability tests in the London Section of the Society of Chemical Industry[4] and the above-mentioned highly important paper by Professor W. Will, printed for private circulation by the New Babelsberg Central Station for scientific technical investigations in December, 1900, were equally too late for the purposes of my own investigation, but they would not have affected it to a great extent. It is, however, very important to notice that Will comes to the conclusion that the results obtained by the Abel test (which was employed in reaching my conclusions) are mostly in satisfactory agreement with those obtained by his own test ; *viz.*, estimating the quantity of nitrogen given off by nitrocellulose when being heated to 135° during four hours. This test he considers to be much more indicative of the stability of such products than all tests founded upon the first appearance of nitrous vapors as utilized in all other tests. I believe therefore we have a right to say that the conclusions drawn from the following experiments are based on a trustworthy foundation.

To compare the stability of samples of guncotton prepared with or without "low oxides" of nitrogen, we had first to try how

---

[1] *J. Soc. Chem. Ind.*, 1897, pp. 288, 293 ; *Ztschr. angew. Chem.*, 1897, pp. 233 and 265 ; 1898, p. 1103.

[2] *Ibid.*, 1898, p. 1027.

[3] *Moniteur Scientifique*, 1900, p. 313.

[4] *J. Soc. Chem. Ind.*, 1901, p. 8.

far the methods employed for washing the product affected the heat tests. A properly nitrated sample was washed for three days with cold water, renewed every hour, always removing the previous water by a vacuum filter ; the washing was continued for three days with hot water of about 90° in the same way. Half of this sample (A) was dried in a current of dry air at 40°, the other half (B) in a vacuum desiccator over sulphuric acid. The first (A) stood the Abel test at 70° for 4′15″, the second (B) for 2′1″,—both quite insufficiently. Since Thomas had asserted that his test sometimes yields results entirely opposite to the Abel test, we subjected another sample of the same product to his test, by means of an oil-bath provided with a thermoregulator, but half a minute after the thermometer had marked 92°, a violent explosion occurred, shattering the whole apparatus, and we cannot therefore, in the interest of the safety of the manipulator, recommend the application of Thomas' tests to samples showing a very low Abel test. Where the Abel test yielded a good result, we applied Thomas' test without any accidents.

No better results were obtained by washing during seven days, partly cold, partly hot, with mechanical agitation of the guncotton in the bath. When adding to this treatment another day's washing with hot water, to which a little sodium carbonate was added, so that alkaline reaction existed up to the end, and assuredly no free acid could be left in the fiber, the Abel test went up only to 8′, still quite an insufficient result.

Clearly the cause of this could not be any free acid still present in the guncotton ; one must think of unstable products formed by the action of the acids on foreign substances present in the cellulose or from cellulose itself by secondary action. Will and Lenze[1] have examined many nitrated carbohydrates (which might be thought of in this respect) for their stability, and found them generally very unstable ; some of these, even when previously insoluble in water, would be removed by boiling with water for some time, which is an operation always carried out in manufacturing guncotton on the large scale.

Lenk and Cross[2] remove such foreign substances by means of acetone, diluted with water to such an extent that it does not dissolve the guncotton itself, and they thus obtain an Abel test up

---

[1] *Ber. d. chem. Ges.*, 1898, p. 68.

[2] *J. Soc. Chem. Ind.*, 1900, p. 642.

to fifty-five minutes. This is no doubt correct but we succeeded quite as well in reaching that limit without the above treatment by merely boiling with water during three days.

We therefore proceeded in all further experiments as follows: After washing out most of the acid with cold water, the guncotton was cut into minute fragments (to imitate the action of the pulping engine) and boiled for several days with frequently renewed water, and we thus attained a sufficient degree of stability. It is unnecessary to say that we had started with highly purified cotton wool, and no fatty matters or other accidental impurities could influence the stability of the product.

The following comparative tests were made with this guncotton.

No.	Temperature of test.	Abel test.	Guttmann test.	Thomas test.
1	66°	17'-15'	24'-23'	3 to 2½ days.
2	70	13'-14'	19.5'-20'	
3	80	6'-6'	10'-12'	

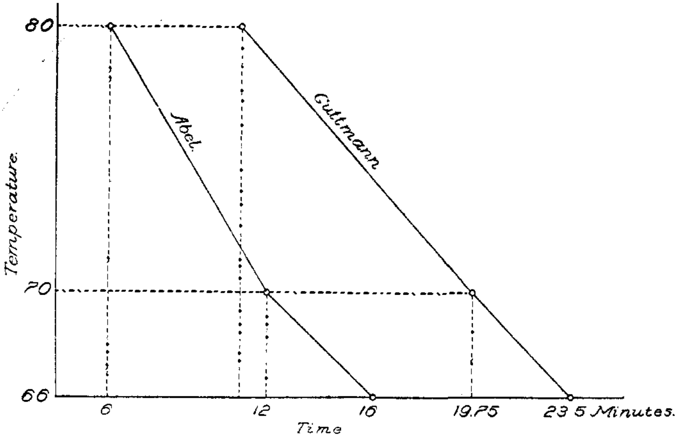

Diagram 3.

The tests No. 1, 2, and 3 were made at different times; when made simultaneously, the tests agreed even better than the above. There is a distinct parallelism between Abel's and Guttmann's tests, although the absolute values are naturally different, owing to the difference in the sensitiveness of the reagents. This parallelism comes out very well in the graphical delineation of the results as shown here.

Evidently we might have employed either Abel's or Guttmann's test for our purpose, as we had nothing to do with the ingredients masking the former; and as the final point is rather better marked in the former than in the latter, we adhered to Abel's test.

In order to apply it to the question to be decided, a number of precisely parallel experiments was made, with the only difference that in each case one nitration was made in the absence of nitrogen tetroxide, the other in the presence of certain quantities of such. The acid mixtures were always the same; the operation was carried out at the same time, the products being washed and dried precisely in the same way and tested in the same water-bath. Unless such absolute parallelism is kept up, the results may vary and may be deceptive, as proved by a number of preliminary experiments.

Series I.—The nitrating mixture consisted of 3 parts sulphuric acid (sp. gr. 1.84), and 1 part nitric acid (sp. gr. 1.52). Half of it was mixed with 4.93 per cent. nitrogen tetroxide, estimated by titrating the mixture with potassium permanganate, and a sufficient quantity of pure nitric acid was added to the other half to represent the HNO_3 formed from N_2O_4 according to the reaction:

$$N_2O_4 + H_2SO_4 = HNO_3 + SO_5NH.$$

The products obtained by nitrating cellulose with both mixtures at the same time, were freed from acid by pressing, cold washing, cutting up most finely, boiling with frequently renewed water for four days, pressing and drying for six days in a vacuum desiccator. Each time a sample of known quality (kept in the damp state and dried immediately before the experiment) was tested along with the other samples in order to make sure of the unchanged sensibility of the test-paper. Usually the time and temperature of explosion was also ascertained by heating 0.01 gram in a test-tube in an oil-bath. The samples left over from testing were taken out of the test-tube, spread on large watch-glasses protected against dust, and the test repeated after some time.

For each test 1.2 grams dry guncotton were weighed out and each sample tested in duplicate, all four being heated at the same time in the same water-bath.

RESULTS.

Date of test.		Without nitrogen tetroxide.		With nitrogen tetroxide.		Check sample for controlling the test-paper.
		a′	a″	b′	b″	c
Dec. 5, 1899.		25′	27′	37′	36′	14
	Expl.	188.5°		188°		195°
	Time	5′11″		5′10″		6′
Jan. 12, 1900.		44′	45′	52′	50′	13′
	Expl.		187°		186°	201°
	Time		5′35″		5′33″	4′30″
March 6, 1900.		55′	54′	64′	64′	
	Expl.	187°		186.5°		196°
	Time	5′30″		5′29″		6′

The first line always shows the time required for the Abel test at 80°; the second the explosion temperature; the third the time elapsing before an explosion occurs.

The Thomas test showed for samples *a*, two and one-half days; for samples *b*, three days; for samples *c*, three days.

The result was *that in each case the guncotton prepared with nitrogen peroxide showed a distinctly better Abel test than that prepared without nitrogen tetroxide.* Of course, I am far from generalizing this, but I am bound to state the fact as found. The explosion of the first kind of guncotton (samples *b*) certainly took place a few seconds before samples *a*, and at 0.5° or 1° lower temperature, but this does not appear to be an appreciable difference. The second explosion could not have been brought about by the first, for the samples *c* throughout maintain their distance from *a* and *b*, although heated in the same oil-bath. It should be noted that there is no parallelism between the Abel test and the explosion test; the samples *c*, strongly inferior as to the former, required a considerably higher temperature for explosion.

The fact that the repetition of the test after an interval of one or two months always yielded higher results, may possibly be explained by the slight loss of nitrogen during the testing. However, it is remarkable that the stability was not diminished, but considerably *raised*, by repeatedly heating to 80°.

The Thomas test also came out better for the guncotton prepared with nitrogen tetroxide than for the other kind.

Series II.—The addition of nitrogen tetroxide was now raised to 9.28 per cent. In this case we wished to determine also the yield, for which purpose the mass, each time when the water was to be removed, was poured through a paper filter attached to a vacuum pump, while in Series I, where porcelain funnels with sieve-plates and filter-pumps were employed, the guncotton remained perfectly white; in Series II, a small quantity of brown matter collected at the bottom of the filter, and in the Abel test the test-paper was deeply stained after three minutes. This bad result could be referred only to the brown matter just mentioned. This was removed by repeating the boiling several times, and this time again passing the mass through a porcelain sieve, which allowed the brown substance to pass through, together with a few fibers of guncotton, both settling out from the filtrate. The quantity of the brown matter was too small for detailed investigation; it decomposed at 193°, with carbonization, but without explosion; it was insoluble in dilute acetone, and hence not identical with the substance to which Lenk and Cross attribute the instability of guncotton. This brown matter appeared in both cases, *a* and *b*, and has consequently nothing to do with the nitrogen tetroxide. It was probably formed by local overheating of fibers carried to the upper part of the flask during the boiling. The guncotton after the last described treatment was perfectly white and of sufficient stability.

This time the tests were carried through twice over (A and B) at different times, each time with two samples, exactly as in Series I, the water-bath being kept at 80°.

A.

	Samples without N_2O_4.		Samples with N_2O_4.		Check sample for paper
Date of test.	*a′*.	*a″*.	*b′*.	*b″*.	*c*.
Jan. 7, 1900.	15′	14′	17′	18′	15′
	Expl. 186.5° Time 4′ 1″		186° 4′		199° 5′ 40″
Jan. 26, 1900.	37′	40′	41′	47′	15′
		Expl. 1.86° Time 4′ 42″		185.5° 4′ 40″	
March 13, 1900.	48′	47′	45′	51′	14′
	Expl. 190° Time 3′ 36″		188° 3′ 34″		

B.

	Samples without N_2O_4.		Samples with N_2O_4.		Check sample for paper.
Date of test.	*a′*	*a″*.	*b′*.	*b″*.	*c*.
Jan. 5, 1900.	15′	13′	15′	12′	16′
	Expl. 186.5° Time 4′ 26″		186° 4′ 25″		201° 4′ 20″

Date of test.	Samples without N_2O_4. a′	Samples without N_2O_4. a″.	Samples with N_2O_4. b′.	Samples with N_2O_4. b″.	Check sample for paper. c.
Feb. 3, 1900.	36′	34′	34′	35′	15
	Expl. 186.5°			185.5°	
	Time 5′ 2″			5′	
March 13, 1900.	47′	49′	51′	56′	15
	Expl. 191°		190.5°		
	Time 3′ 5″		3′ 4″		

Both Series II, A, and II, B, agree with the results of Series I in showing that the presence of nitrogen tetroxide does not lower the Abel test, in the raising of the test on repetition, and in the minute difference of the explosion temperatures. It is also interesting to note that the results of Series II, A and B, although carried out at different times, agree excellently with each other.

The nitrogen percentage of sample *a* was 13.04, of sample *b* 13.09, both practically the same, but somewhat lower than the acid mixture employed would have yielded without the prolonged boiling; *viz.*, 13.35 to 13.42. Guttmann[1] notices this lowering of the nitrogen percentage by boiling on the large scale, while Bruley,[2] after 260 hours' boiling, found a diminution of only 1 cc. NO = 0.06 per cent. nitrogen.

Series III.—Since in the last series we had not handled guncotton of the highest percentage, owing to the three days' boiling, we prepared a new sample with only one day's cold washing and four hours' boiling. It showed 13.37 to 13.35 per cent. nitrogen, which is quite equal to a good commercial guncotton. The stability test yielded.

Date of test.	Without N_2O_4.	With N_2O_4.
June 21, 1900.	3′ - 3′ 20″	3′ - 3′ 40″
July 4, 1900.	4′ - 4′ 15″	4′ - 4′ 19″
	Expl. 166°	164°
	Time 3′52″	3′ 50″

The stability is low, but again *there is no difference in favor of the product made without nitrogen tetroxide.*

Ultimately we tested for solubility, because Payen had asserted that the guncotton made in the presence of nitrogen tetroxide is soluble in ether-alcohol; that made without nitrogen tetroxide insoluble. We found absolutely no difference in this respect, and Payen's statements of the year 1847 must therefore be altogether excluded from further consideration.

---

[1] "Schiess und Sprengmittel," p. 85.

[2] *Mém. des poudres et salpêtres*, **8**, 131.

The above shows that nitrogen tetroxide, when added to a mixture of strong sulphuric and nitric acids, even up to the enormous amount of 9.28 per cent., has no such deteriorating action on the stability of guncotton as is generally assumed. But for the sake of completeness it may be mentioned that free nitrogen tetroxide, in the liquid form, has a destructive action on cellulose. 100 grams liquid nitrogen tetroxide, acting on 8 grams pure cotton during three days in the ice-safe, converted it into a viscid mass, the fibers being strongly enlarged, and mostly soluble in boiling water. The solution reduces Fehling's solution on boiling and gives precipitates with phenylhydrazine (insoluble in the ordinary organic solvents) as well as with lead, silver, and barium salts.

I believe this fully justifies the conclusion that *nitrogen tetroxide* ("low oxides") *in the nitric acid, even far beyond the proportion ever found in commercial acids, has no injurious action in the manufacture of guncotton, neither toward nitrogen percentage, yield, nor stability as measured by the ordinary tests.* I should have liked very much to approach the same question for *nitroglycerine*, which may or may not behave in a way similar to nitrocellulose ; since the prejudice against nitrogen tetroxide has proved to be wrong in one case, it might possibly be so in the other case. But I must leave this task to others ; the handling of *nitroglycerine* is so much more dangerous than that of nitrocellulose that I did not feel justified in undertaking such work in a public laboratory where hundreds of students congregate.

I. Behavior of Different Commercial Grades of Cotton in Nitration, Especially for the Manufacture of Collodion Cotton.

All our researches had been made with the same material, *viz.*, the purest form of cellulose obtainable in the shape of " surgical cotton wool," which is, of course, much too expensive for manufacturing commercial nitrocelluloses.

In ordinary practice good cotton waste, mechanically purified, and boiled in alkaline solutions, is the material of the manufacturer. Of course this cotton waste belongs to many different commercial grades of cotton, and some practical men believe that their failure to obtain uniform products is caused by differences in the original cotton. Especially it is believed that this accounts for the alleged " fact " that by the same mixture of acids (?)

sometimes a soluble, sometimes a difficultly soluble, collodion cotton is obtained.

Looking at the complicated structure of the cellulose molecule on the one side, and at the greatly varying morphological structure of the vegetable fiber, even that of various species of cotton fiber, on the other side, it cannot be denied that there is some *prima facie* reason for the above assumption.

Nettlefold[1] obtained different products when nitrating wood fiber and cotton by the same acid mixture ; the former yielded a product with 11.2 per cent. nitrogen, and 41.6 per cent. soluble matter ; the latter yielded the highest degree of nitration and only 8 per cent. soluble matter. I am not aware whether wood fiber ("cellulose" of the German manufacturer, made by various processes, *viz.*, the soda, sulphate, and sulphite processes) is anywhere used in the manufacture of collodion cotton, but even when confining ourselves to ordinary cotton, there might have been something in the opinion that various grades of this would behave differently in the nitrating process. Indeed I must confess that I started from this as the most probable assumption.

In order to bring it to a test, I procured from the leading cotton mills in Switzerland authentic samples of the most varying grades of cotton, which were carefully cleaned mechanically and washed in the same way as in the manufacture of guncotton and nitrated with the same acid mixture (63.84 sulphuric, 16.96 nitric acid, 19.20 water), keeping all the conditions of the experiments exactly alike. Together with these we nitrated a sample of our "chemically pure surgical cotton wool," with the following results:

No.	Commercial designation.	Nitrogen. Per cent.	Solubility in ether-alcohol. Per cent.	Yield. Per cent.
1.	Chemically pure surgical cotton wool	11.76	100	159
2.	American cotton "middling fair"...	11.56	100	157
3.	American cotton "Florida"	11.67	100	153
4.	Egyptian cotton, white, "Abassi" ..	11.69	100	155
5.	Egyptian cotton, natural yellow.....	11.61	100	154

This shows that, contrary to my own assumption, *there is no essential difference in the quality of the collodion cotton obtained from these extremely differing grades of cotton.* They are all completely soluble; the nitrogen differs only by 0.13 per cent. among all the commercial cottons, and only by 0.20 *in maximo* against

---

[1] *Chem. News*, **55**, 306.

the pure surgical cotton. The latter is easily explained by the difference in purity, the surgical cottons containing only 0.05 per cent. ash, the commercial cottons averaging 0.5 per cent. ash, but this is evidently quite immaterial for manufacturing purposes.

The varying results observed in manufacturing nitrocellulose, especially collodion cotton, must therefore *not* be attributed to variation in the quality of the cotton employed, but most probably to unequal conditions of nitration, perhaps as regards temperature, but most probably as regards differences in the percentages of water contained in the acid mixture, which may have been overlooked by the manufacturer. The preceding investigation shows that even very slight differences in the percentage of water may be of the greatest importance for the result, more important than even much greater differences in all other respects.

ZURICH, May, 1901.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 57.]

THE ELECTROLYTIC SEPARATION OF MERCURY FROM COPPER.

BY C. ROSCOE SPARE AND EDGAR F. SMITH.

Received June 25, 1901.

AT intervals, since the electrolytic separation of mercury from copper was first announced, statements have appeared that the separation was unsatisfactory. The first objection was to the length of time consumed, but it was soon observed in this laboratory that this factor was very materially reduced upon heating the electrolyte to 65° C. Then it was said that the separation was only applicable and satisfactory when the quantity of copper was not too large, as compared with the amount of mercury in the solution. Proper replies were made to these restrictions upon the method, but recently another chemist, in the person of Emil Goecke, published in his inaugural thesis "Ueber den Genauigkeitsgrad elektro-analytischer Arbeitsmethoden," etc., that he not only required from sixteen to twenty-four hours to effect the separation, but that in only three instances did he find the mercury free from copper. It is not the purpose of the writers to question Goecke's ability to conduct electrolytic work, or analytical work of any kind for that matter, but they feel that it is only fair to lay additional actual experience before the reader, leaving time and further trials to determine finally who is right.