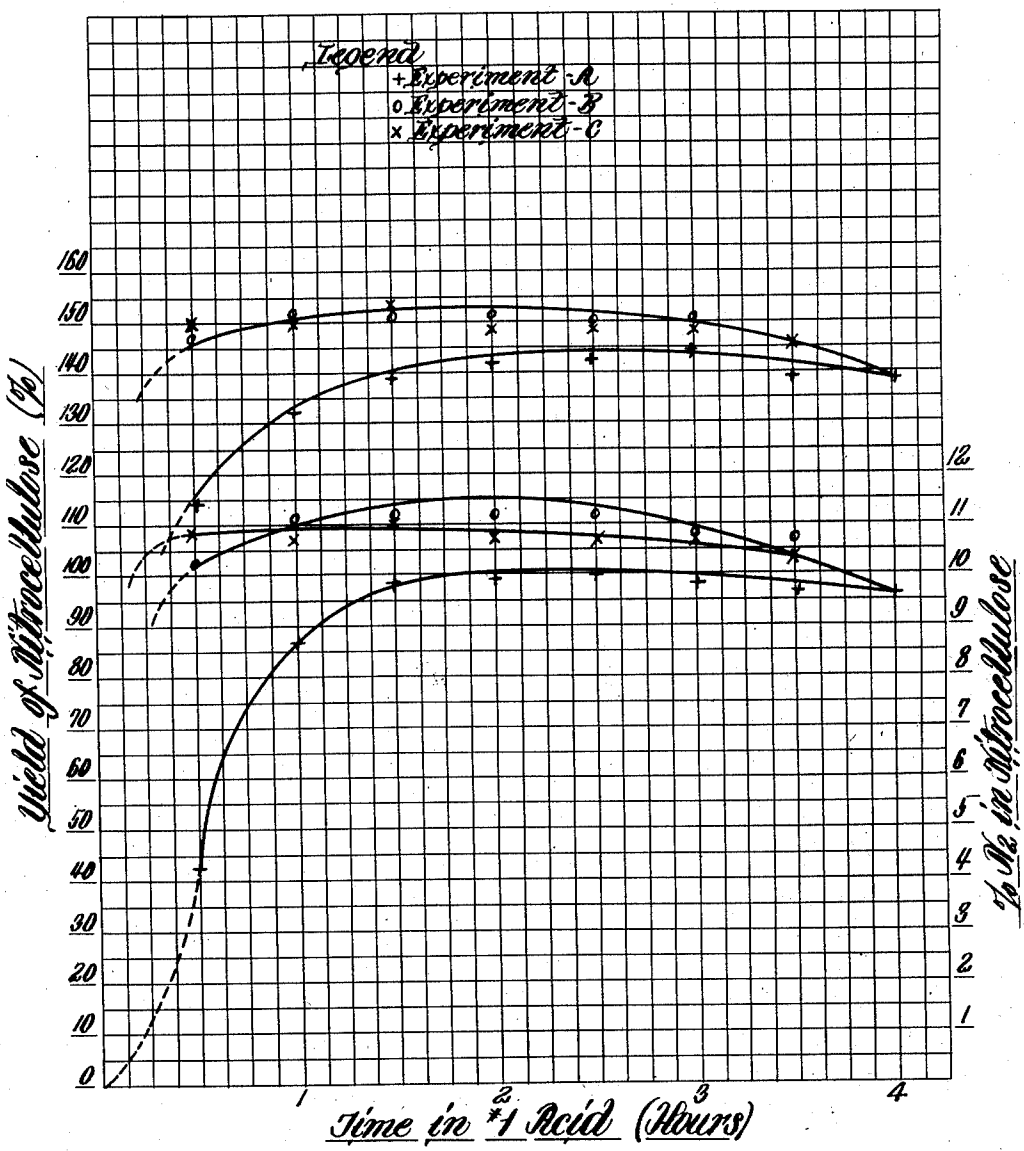
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PRODUCTION OF NITROCELLULOSE

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PRODUCTION OF NITROCELLULOSE

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This invention is directed to the production of nitrocelluloses of all varieties, such as used, for example, as raw material in the manufacture of plastics, lacquers, films, artificial silk, explosives, and kindred products.

When cellulose is nitrated, it is steeped in a mixed acid, consisting essentially of nitric acid, sulphuric acid, and water. It is well known that the proportions of cellulose, nitric acid, sulphuric acid, and water all play an important part in establishing the characteristics of the nitrocellulose produced, that is, the nitrogen content, the yield, the clarity of solutions of the nitrocellulose in solvents, and so on. It is also known that the physical form of the cellulose during nitration is an important factor in determining the course of the reaction.

After considerable investigation of nitration problems, I have discovered that marked advantages may be realized by carrying out the nitration of cellulose in two or more stages, the first-stage nitration being effected with an acid rich in nitric acid, and the second-stage nitration with an acid less rich in nitric acid. While not restricted thereto, such a discovery may be applied most profitably when the cellulose is in the form of comparatively thick sheets of unbeaten wood pulp, such as the so-called "drier sheets" available on the market for viscose-rayon manufacture. Heretofore the nitration of such sheets was attended by many serious obstacles, even when the pulp was refined to high alpha cellulose content and was reasonably expected to give good results. Thus, if such sheets are allowed to undergo nitration to completion in the usual nitrating acid at normal temperatures, hydrolysis takes place to such an extent that the yield is inordinately low; the sheets tend to disintegrate; the acid retained by the nitrocellulose is excessively high; and the nitrocellulose is comparatively non-uniform and otherwise lacking in optimum characteristics. By applying the principles of the present invention, however, drier sheets as thick as 0.040 inches, or even greater, may be satisfactorily nitrated in two to four hours at temperatures as high as 30° or 40° C., or even higher.

The use of unbeaten wood pulp in the form of thick sheets for the direct production of nitrocellulose constitutes an economic advantage of the first magnitude, as it does away with the necessity of employing comparatively expensive steps, such, for instance, as those required in making tissue or shredded fiber,—forms of cellulose heretofore believed necessary for best nitration results. The production of thick sheets of unbeaten wood pulp, say, 0.020 to 0.050 inches thick, is carried out at comparatively low cost at a pulp mill where it is customary practice to pump the finished pulp to so-called pulp driers, which are built as large units capable of handling at low cost 150 to 200 tons or more of fiber per day. Again, the washing, stabilizing, dehydrating and other after-nitration treatments may be carried out economically on the sheet nitrocellulose, which is easy to handle and which is a compact and convenient form in which to store and ship nitrocellulose.

In carrying out the process of the present invention, I may use as the first-stage nitrating acid one which is unusually rich in nitric acid but of substantially normal water content. If the acid is maintained at, say, 30° C., and the sheets are allowed to remain steeped in the acid until an equilibrium nitrogen content is reached, the product will have a nitrogen content short of that desired in the final product, say, about 10%, but the sheets will be substantially uniformly and completely nitrated. One may proceed from this step product, or from one which has not yet reached an equilibrium nitrogen content to a comparatively uniform final product having a nitrogen content of, say, about 11.5%, and other characteristics desired, by

steeping, by way of example, the sheets constituting the step product in an acid whose composition is or approximates that of the usual nitrating acid.

The initial-stage nitrating acid may be one whose sulphuric acid to nitric acid content ratio is less than about 2 to 1, while that of the second-stage nitrating acid is greater. For instance, this ratio may be, say, 1 to 1, or 1.5 to 1 in the initial-stage nitrating acid and, say, 3 to 1 in the second-stage nitrating acid. After the initial-stage nitration has been effected, the acid used therefor may be drained from the nitrating vat and be replaced by the second-stage nitrating acid. The initial stage nitration may be carried on for, say, one-half to two hours, and the final-stage nitration for, say, two hours. The total time consumed is thus reasonably short, so that the nitrating acid and nitrating equipment is not unduly tied up in a single nitration.

In carrying out my process on a commercial scale, the sheets may be supported vertically in closely spaced, parallel relation, as in frames; or they may be suspended as from glass rods or clamps. The sheets should be lowered sufficiently in the vats to permit the baths of nitrating acid to cover them completely, their spaced relation permitting uniform access of acid to all the surfaces of the sheets. Other modes of carrying out the two-stage nitration of the present invention may, however, be employed without departing from the spirit or scope of invention as defined in the appended claims.

While I find it difficult to account with precision for the results made possible by a two-stage nitration such as described, nevertheless there are certain known factors which probably underlie and are responsible for these results. For instance, it has been observed that the acid used in the first-stage nitration has a comparatively slight gelatinizing or hydrolyzing effect on the sheets under the temperature conditions used. This may be due to the fact that the initial stage nitrating acid is of considerably lower viscosity than the usual nitrating acid, and accordingly that it penetrates into the sheets rapidly to produce a high nitric acid concentration throughout the sheets, which permits of nitration to an equilibrium nitrogen content without the occurrence of undesirable side reactions. This equilibrium nitrogen content is lower than that desired in the finished product, by reason of the fact that, other things being equal, with ratios of sulphuric acid to nitric acid less than, say, 3 to 1, lower degrees of nitrogen in the nitrocelluloses results than if higher ratios are used. Hence, after the initial stage nitrating operation, the porous sheets are filled with an acid mixture which is in equilibrium with a comparatively low nitrogen content nitrocellulose. In the final stage of nitration, where the nitrating acid is comparatively rich in sulphuric acid, the residual acid in the pores of the sheets resumes reaction gradually and smoothly as it gradually receives sulphuric acid by diffusion from the pool of nitrating acid used in the second stage. In other words, the second stage nitrating acid mingles in the pores of the sheets with the residual acid from the previous treatment, which is sufficiently strong to prevent side reactions, so that the nitration of the sheets proceeds smoothly to completion.

In some cases, it may be desirable to treat the sheets for a comparatively short period of time with a nitrating acid of a composition corresponding to that used in the second-stage nitration, before the first-stage nitration is effected. This initial treatment is of sufficiently short duration so that before the acid within the superficial pores of the sheets reaches the hydrolyzing stage, it is drained off and the nitric-acid-rich, more fluid, first-stage nitrating acid is added. Such an initial treatment, which may be in the nature of a five-minute dip, is of advantage, in that it makes possible the use of a wide variety of acid compositions in the first nitrating stage, without running into the danger of producing a final product tending to give hazy nitrocellulose solutions. The choice of a first-stage nitrating acid of the proper composition does not give rise to the foregoing trouble, but there are some acid compositions that do. The nitration of the outer layers of the sheets to completion before the first-stage nitration ensures the production of nitrocelluloses which give clear nitrocellulose solutions.

I shall now give typical procedures falling within the purview of the present invention. In these examples, a refined wood pulp of high alpha cellulose content was employed as a raw material. The pulp was in an unbeaten condition and in the form of drier sheets 0.040 inches thick and weighing 450 grams per square meter. In one case, the sheets were submerged in fifty times their weight of a nitrating acid at 40° C., of the following composition:

Water	18.7%
HNO_3	40.6%
H_2SO_4	40.7%

After two hours, the acid bath was drained from the sheets and a second nitrating acid at 40° C., of the following composition, was added:

Water	18.7%
HNO_3	20.5%
H_2SO_4	60.8%

After another two hours, the second nitrating acid was drained from the sheets, whereupon the sheets were weighed for acid retention, then were drowned in a bath of water and after several rinses were placed in boiling

water for two hours, where they were stabilized. They were then dried and found to be in an integral, firm condition. It was found that they had increased 53% in weight, that they had an average nitrogen content of 11.5%, and were completely nitrated. The acid retention was 1.4 pounds of acid per pound of nitrocellulose.

In another case, a first-stage nitrating acid of the following composition was used:

Water	17.0%
HNO_3	33.2%
H_2SO_4	49.8%

Other conditions of the previous case were maintained, but both acid baths were kept at 30° C. In this case, the yield of dry nitrocellulose obtained was 1.56 times the weight of the original dry cellulose, and the average nitrogen content was 11.4%. The acid retention was 1.38 pounds of acid per pound of nitrocellulose. Solutions of the acidified and stabilized nitrocellulose in acetone and in amylacetate were clear and homogeneous. It is to be noted that in this case the ratio of sulphuric acid to nitric acid in the first-stage nitrating acid was 1.5 to 1, rather than 1 to 1, as in the case previously given.

The foregoing examples are typical of a wide variety of times, temperatures, and compositions of nitrating acid which may be used in a process such as described, but in any case the principle of using a nitrating acid rich in nitric acid in the first stage, and a nitrating acid containing a high ratio of sulphuric acid to nitric acid in the second stage to complete nitration, is applied.

In order to arrive at a nitrocellulose of a given nitrogen content, it is well known in the art that nitrating acid of a definite nitric acid to sulphuric acid ratio should have a predetermined water content. As the ratio of one acid to the other varies, the water content necessary to produce a nitrocellulose of the same nitrogen content may vary within relatively narrow limits. Generally speaking, the amount of water present in nitrating acids may be from, say, 12% to 23% depending upon the nitrogen content and other characteristics desired in the nitrocellulose, but it is to be understood that the range of water content may also vary, depending upon many factors, including ratio of one acid to the other, the nature of the cellulose, the temperature of nitration, the ratio of nitrating acid to cellulose in the bath, etc.

In order to show the progress of the reaction in a two-stage nitrating process such as described in the examples cited, the curves plotted on the accompanying drawing are submitted. The ordinates of the lower three curves represent the per cent. nitrogen in the product, and the abscissæ represent the time of immersion in hours in the first-stage nitrating acid. The ordinates of the upper two curves represent the yield of nitrocellulose in per cent., the uppermost of these two curves being for two experiments. The nitrogen and yield curves marked "Experiment A" were plotted from the results obtained by steeping drier sheets of the kind previously described in a nitrating acid at 40° C., of the following composition:

Water	18.7%
HNO_3	40.6%
H_2SO_4	40.7%

The curves marked "Experiment B" were plotted from the results obtained by taking step products, after various lengths of time in a first-stage nitrating acid of the composition just given, and steeping them for various lengths of time in a second-stage nitrating acid at 40° C., of the following composition:

Water	18.7%
HNO_3	30.6%
H_2SO_4	50.7%

Experiment C was carried out under the same conditions as Experiment B, except that the second-stage nitrating acid was maintained at 20° C. I present herein the tabulated values of the three experiments from which the curves were drawn:

Experiment A

Time in No. 1 acid	Yield	Percent nitrogen	Appearance in acetone
½ hr.	114.5	4.25	Large amount insoluble
1 hr.	132.2	8.63	Moderate amount insoluble
1½ hrs.	139.0	9.70	Small amount insoluble
2 hrs.	142.0	10.10	Small amount insoluble
2½ hrs.	142.3	9.97	Small amount insoluble
3 hrs.	143.8	9.87	Solution turbid
3½ hrs.	139.0	9.73	Solution turbid
4 hrs.	138.0	9.92	Solution very turbid

Experiment B

Time in No. 1 acid	Time in No. 2 acid	Yield	Percent nitrogen	Appearance in acetone	Appearance in amyl acetate solution
½ hr.	3½ hrs.	146.2	10.29	Clear	
1 hr.	3 hrs.	151.2	11.15	Clear	Clear
1½ hrs.	2½ hrs.	151.5	11.18	Clear	Clear
2 hrs.	2 hrs.	151.9	11.28	Clear	
2½ hrs.	1½ hrs.	150.2	11.27	Clear	
3 hrs.	1 hr.	150.0	10.78	Clear	
3½ hrs.	½ hr.	147.5	10.72	Clear	
		140.2	9.28		

Experiment C

Time in No. 1 acid	Time in No. 2 acid	Yield	Percent nitrogen	Appearance in acetone	Appearance in amyl acetate solution
½ hr.	3½ hrs.	150.0	10.86	Clear	Clear
1 hr.	3 hrs.	150.1	10.68	Clear	Clear
1½ hrs.	2½ hrs.	152.2	11.08	Clear	Clear
2 hrs.	2 hrs.	148.6	10.72	Clear	Clear
2½ hrs.	1½ hrs.	148.2	10.74	Clear	
3 hrs.	1 hr.	148.0	10.69	Clear	
3½ hrs.	½ hr.	146.9	10.46	Clear	
		141.4	9.80		

In the case of the three experiments, the

total time of nitration was four hours. The sheets used as a raw material in these experiments were initially dipped in an acid of a composition similar to that of the second-stage nitrating acid, but the period of immersion was only five minutes, so that only the surface cellulose was nitrated. The curves remain practically the same if the initial dip is omitted, except at their starting portions, which are unimportant for practical purposes. From the plotted results, it is apparent that the second-stage nitration increases the yield and actually takes part in the nitration. It is further apparent that the nitrogen content of the nitrocellulose produced may be varied by varying the durations of the treatments in the first-stage and second-stage nitrating acids, but in ordinary practice, if it is desired to produce a finished nitrocellulose of about 11.5% nitrogen content, the step product of the first nitration, which has a nitrogen content of less than about 11.5%, is nitrated in the second-stage acid for a sufficient period of time to convert the step product into a finished product of the nitrogen content desired.

The economic advantages of the process herein described are of high significance. Not only are yields of nitrocellulose obtained from comparatively thick sheets of unbeaten wood pulp comparable to those obtained when cotton linters is used as the raw material, but the acid losses are very low. Since the nitrating temperatures are comparatively high, say, 30° to 40° C., or even higher, a wide range of viscosities of nitrocellulose is made possible. Because of the comparatively compact nature of the sheets, it is possible to get a comparatively high ratio of cellulose to nitrating acid in the nitrating vats,—much higher, if desired, than when tissue, linters, or shredded pulp is used, so that, aside from the fact that the raw material is handled in its cheapest form, the nitrating equipment is of the simplest kind, and the labor cost of the process is relatively small.

I claim:

1. A process which comprises the nitration of thick sheets of unbeaten wood pulp at temperatures as high as 30° to 40° C., substantially without side reactions.

2. A process which comprises the nitration of sheets of substantially unbeaten wood pulp at temperatures as high as 30° to 40° C., while maintaining the integrity of the sheets.

3. A process which comprises steeping cellulose in a nitrating acid in which the ratio of sulphuric acid to nitric acid is less than 2 to 1, and then steeping the cellulose in a nitrating acid in which the ratio is greater.

4. A process which comprises steeping thick sheets of unbeaten wood pulp in a nitrating acid in which the ratio of sulphuric acid to nitric acid is less than 2 to 1, and then steeping the sheets while wet with such acid in another nitrating acid in which the ratio is greater.

5. A process which comprises treating cellulose with a nitrating acid in which the ratio of sulphuric acid to nitric acid is between 2 to 1 and 1 to 1, and then with a nitrating acid in which the ratio is greater than in the first nitrating acid and greater than 1 to 1.

6. A process which comprises treating cellulose until partially nitrated with a nitrating acid sufficiently rich in nitric acid to avoid material loss through side reaction, and then treating the partially nitrated cellulose with a nitrating acid richer in sulphuric acid content.

7. A process which comprises nitrating only the surface of thick sheets of cellulose with one acid, nitrating the bulk of the remainder of the sheets with a second acid, and then nitrating with an acid similar to the first.

8. A process which comprises immersing thick sheets of cellulose in a bath of nitrating acid to nitrate only the surface of such sheets, then immersing such sheets in a bath of nitrating acid richer in nitric acid, and then in a bath similar in composition to that used in the first bath.

9. A process which comprises treating thick sheets of cellulose with a nitrating acid in which the ratio of sulphuric acid to nitric acid is greater than 1 to 1 to nitrate only the surface of the sheets, then with an acid richer in nitric acid to nitrate the rest of such sheets, and finally with an acid in which the ratio is greater than 1 to 1 to increase the nitrogen content of said rest of the sheets.

10. A process which comprises steeping cellulose in a succession of baths of nitrating acid, both the nitric acid content and the nitric acid to sulphuric acid ratio of one bath being markedly higher than that of a succeeding bath, and effecting a step-by-step nitration of said cellulose from the first bath into which it is introduced to the last bath from which the desired nitrocellulose is removed.

11. A process which comprises steeping a wood fiber of high alpha cellulose content in a plurality of baths of nitrating acid of different compositions, both the nitric acid content and the nitric acid to sulphuric acid ratio of one bath being markedly higher than that of a succeeding bath, and effecting a step-by-step nitration of said wood fiber from the first bath into which it is introduced to the last bath from which the desired nitrocellulose is removed.

12. A process which comprises steeping thick sheets of cellulose in a plurality of baths of nitrating acid of different compositions, both the nitric acid content and the nitric acid to sulphuric acid ratio of one bath being markedly higher than that of a succeeding

bath, and effecting a step-by-step nitration of said sheets from the first bath into which they are introduced to the last bath from which the desired nitrated sheets are removed.

In testimony whereof I have affixed my signature.

MILTON O. SCHUR.