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MATERIAL FOR CONVERSION INTO CELLULOSE DERIVATIVES AND PROCESS OF PRODUCING THE SAME

No Drawing. Application filed October 9, 1926. Serial No. 140,675.

This invention relates to the conditioning of cellulosic material for conversion into cellulose derivatives. It is especially concerned with cellulosic material conditioned for conversion into cellulose derivatives and, more particularly the lower nitrocelluloses, such as those customarily utilized in the manufacture of lacquers, films, artificial silk, celluloid products, and their congeners.

Although the process herein disclosed may be practised advantageously with cellulosic materials of all kinds, it is applied most expediently to the conditioning of paper prepared from chemical wood pulp, particularly refined wood pulp containing a high percentage of alpha or resistant cellulose. Such high alpha cellulose fiber may be converted into cellulose derivatives having physical and chemical properties comparable to those prepared from cotton fiber or cotton linters, in contrast to the relatively impure derivatives having inferior properties prepared from chemical wood fiber of lower alpha cellulose content. The high alpha cellulose fiber may be produced as described in application for patent, Serial No. 72,522, filed December 1, 1925, by George A. Richter and Milton O. Schur, by treating a raw or unbleached fiber, e. g., sulphite fiber, containing, say, about 85% to 87% alpha cellulose, under proper temperature conditions, in a solution of caustic soda or equivalent alkaline agents of suitable concentration. During such treatment, certain non-alpha cellulose constituents present in the fiber, such as the beta and gamma celluloses and ligneous and coloring material, are dissolved, so that after the requisite period of treatment there results a refined or purified fiber containing about 93% alpha cellulose. The refined fiber requires a relatively small amount of bleach for conversion into a fiber of high whiteness, usable as a new rag or cotton fiber substitute in the manufacture of bond, ledger and writing papers of the finest quality and in the preparation of cellulose derivatives of high commercial value and purity. It may be desirable, especially if the raw fiber contains a percentage of non-alpha constituents higher than usual, to pretreat the fiber with an oxidizing solution, e. g. a chlorine solution, to remove a portion of such constituents or to facilitate their removal by subsequent treatment in the alkaline solution.

If a fiber of very high alpha cellulose content, say, 95% to 98%, is desired, the alkaline treatment may be succeeded by a second alkaline treatment, as described in application for patent, Serial No. 75,888, filed December 16, 1925, by George A. Richter. By a double alkaline treatment, the quantity of bleach required to produce fiber of high whiteness is materially reduced. The refined fiber serves as an excellent raw material for the preparation of cellulose derivatives.

If cellulose fiber, and more particularly a refined wood fiber—which for convenience of designation will be termed "alpha fiber"—is conditioned for nitration by mercerization in a solution of caustic soda, as described, in application for patent, Serial No. 140,677, filed October 9, 1926, by George A. Richter, Milton O. Schur and Royal H. Rasch, the nitrating characteristics of such fiber are markedly improved. The fiber may be mercerized while in any suitable state, but we have now found that optimum results are realized when the fiber, preferably beaten to a material extent, is mercerized in paper form, and the mercerization is followed by a treatment with hot alkaline water.

In the past, great difficulty has been experienced in the nitration of chemical wood pulp. If fiber containing, say, 88% alpha cellulose is nitrated, the lacquers or films prepared from the nitrocelluloses are highly colored—a very serious defect for most industrial purposes. When refined wood pulps, i. e. high alpha fiber, are nitrated, this defect disappears, especially if a double alkaline treatment is used in the purification of the wood pulp. On the other hand, the yield of nitrocellulose is low and the acid retention excessive unless the alpha pulp has been materially hydrated prior to nitration as disclosed in application for patent Serial No. 97,998, filed March 27, 1926, by George A. Richter, Milton O. Schur, and Royal H. Rasch, or unless the fiber has been mercerized, as described in application for patent

Serial No. 140,677, filed October 9, 1926, by George A. Richter, Milton O. Schur, and Royal H. Rasch. (Acid retention is the percentage of the weight of original nitrating acid retained by the nitrated pulp when centrifuged under carefully standardized conditions. It is a direct measure of the loss in nitrating acid experienced in usual technical practice when the centrifuged material is drowned in large volumes of cold water.)

Mercerization effects a change in the character of the fiber which upon nitration asserts itself in a lower acid retention, and a higher yield of nitrocellulose product. The product is of high purity and produces a smooth, homogeneous and clear solution in a nitrocellulose solvent, from which better and stronger films and other products may be realized than from solutions formed from unmercerized fiber. One factor contributing to these results doubtless is that during mercerization a further removal of non-alpha cellulose constituents in the alpha fiber is effected, and hence there results a purer nitrocellulose, from which better lacquers, films, or other plastics may be produced.

For the realization of high yields of nitrocellulose, economy in the consumption of the mixed nitrating acids, and the attainment of substantially colorless nitrocellulose products of desired physical characteristics, it is necessary to control the physical condition of the raw material as well as its chemical purity. Our observation is that a change in the structure of the fiber which retards the action of the mixed nitrating acids improves the purity and quality of the product, raises the yield, and lowers the acid retention. This observation is borne out by the fact that an increase of couching pressure before drying, in sheeting the alpha fiber on a paper machine, produces noteworthy advantages in nitration. Or, if the web of alpha fiber is filled with, say, 1% of nitrocellulose, advantages in nitration are observable. These results are further in accord with the disclosure in application for patent, Serial No. 97,998, filed March 27, 1926, by George A. Richter, Milton O. Schur, and Royal H. Rasch, wherein it is set forth that beating or "hydration" of the fiber prior to nitration is accomplished by favorable results. Mercerization appears to effect results similar to beating, and, if desired, may be combined with a beating of the fiber, so that the advantages incident to both may be realized.

Our further conclusion is that, when the pulp is highly absorptive, it is attacked rapidly by the sulphuric acid present in the mixed nitrating acid, partly dissolving or forming unstable esters, which are hydrolyzed and dissolved during subsequent washing of the product, necessarily resulting in a low yield and high acid retention. When the pulp is beaten or mercerized, however, the initial attack by the sulphuric acid appears to be modified and the nitric acid is allowed time to penetrate into the fibers in the proper concentration to form stable nitrates. To secure thorough and uniform penetration of the fibers in a short period of time, the fiber is preferably nitrated in the form of small pieces of thin sheets.

By lowering the reactivity of the cellulosic material, we also decrease the chance for local overheating in the nitrating acid bath. As is well known, an increase in the temperature at which nitration is conducted is generally followed by a decrease in yield of nitrocellulose, particularly with wood cellulose, and, since nitration is a highly exothermic reaction, the chances for local overheating in the pulpy mixture of fibers and viscous nitrating acid are high unless steps are taken to retard the reaction so that the heat evolved may have the opportunity to distribute itself uniformly throughout the entire mass.

Although the necessity of taking into account the physical condition of the fiber in the nitration of wood pulp has lately been generally recognized, we are, so far as we know, the first to discover the advantages to be gained by hydrating the fibers mechanically or chemically prior to nitration. It should be emphasized that, whereas these advantages are of comparatively little importance in the case of unrefined pulps, they are of paramount importance when high alpha pulps are under consideration, for the process of purifying chemical wood pulps increases greatly the porosity or sponginess of the cellular material, causing such pulps, unless hydrated or otherwise treated to reduce absorbency, to give uneconomical results in technical nitration. Thus, for example, when thin sheets of unbeaten (i. e. non-hydrated) sulphite pulp are nitrated with an acid under conditions hereinafter given, a yield of about 145% and an acid retention of 4.5% to 5.5% are noted. Thus, also, a yield of about 150% and an acid retention of about 4.5% are noted when a good grade of cotton linters are similarly treated. Unbeaten alpha pulp, on the other hand, yields but 136% of cellulose nitrate and suffers an acid retention as high as 7.6%.

The applicability of the process of the present invention may best be appreciated by reference to a specific example of procedure such as the following. The alpha fiber for mercerization is preferably in the form of a thin "water-leaf" sheet or nitrating tissue below 20 in basis weight (i. e., the weight of 480 sheets of 24" x 36"), or equivalent to a thickness of approximately .003 inches. The fiber may, for optimum results, be beaten to a greater or less degree prior to its formation into such tissue. The sheet may be treated or steeped from two to five seconds in a caus-

tic soda solution of mercerizing strength, an 18% NaOH solution, for example, at room temperature, say, 68° F. Under such conditions, the desired mercerization of the fiber takes place. The sheet is then "drowned" in water, preferably hot water, the use of which effects a very desirable and important further purification of the cellulose, for the caustic soda absorbed by the sheet dissolves, under the influence of the hot water, impurities incompletely removed by the comparatively cold caustic in the mercerizing bath. The hot water rapidly assumes a deep brown coloration and the purification of the tissue becomes manifest in the enhanced freedom from color in the cellulose nitrate products. The less pure the cellulose to start with, the darker the hot water becomes and the greater the comparative gain in the quality of the cellulose derivatives. Further, the hot water preserves the sheet in a firm integral condition, whereas cold water may cause the sheet to disintegrate into a pulpy mass difficult to handle. The sheet is then neutralized of absorbed caustic soda, by an acid or souring treatment, as in a 20% acetic acid solution, whereupon the sheet may be washed free from acid in cold water, and dried. The resultant sheet tends to crinkle on drying, so that, if the tension usually employed during drying is slightly reduced, crinkled material is obtained, which, when cut up into small pieces and nitrated, has but little tendency to stick together in the nitrating bath or in the centrifuge. The yield on mercerization is 97.2% when carried out for 2 to 5 seconds. If mercerization is carried out for a longer period, the yield is somewhat lower, a mercerization lasting 5 minutes resulting in a 95.0% yield.

It is apparent that by our process two very important ends are simultaneously attained; the fibers are hydrated chemically and are further purified. It is apparent that purification takes place under conditions which leave the dried cellulosic material in a compact state as opposed to the unfavorable spongy, porous condition of chemical wood pulp highly purified in the usual way.

Upon nitrating ¼-inch squares of the mercerized water-leaf tissue which had been prepared from fiber pre-beaten to some extent, we obtained a yield of about 155% and an acid retention of about 3.3%, as compared with a yield of about 145% and an acid retention of 4.3% when nitration was carried out on the same stock, unmercerized. Furthermore, a solution prepared from the nitrocellulose the base of which had been mercerized was clearer, lighter, and less viscous than a solution prepared from the nitrocellulose the corresponding base of which was left unmercerized. In addition, a film made from the first solution, when subjected to test, was materially stronger and had a better appearance than a film made from the second-mentioned solution.

The comparative values hereinbefore given were obtained by the use of a nitrating acid suitable for the preparation of the lower nitrates and consisting of:

HNO_3	20.5%
H_2SO_4	60.8%
H_2O	18.7%

(the ratio of acid used to fiber being 50 to 1). The nitration was carried out at 40° C. for thirty minutes.

The best results, as indicated above, are obtained when the alpha fiber is both beaten and mercerized. A mercerized water-leaf sheet of alpha fiber prepared from beaten fiber yields nitrocellulose, from which films and other products may be prepared, having properties comparable to those obtained with either a good grade of cotton linters or with a moderately high grade rag sheet.

Our mercerized fiber conditioned for nitration has, among others, the following characteristics:

	Per cent
Alpha cellulose content	Over 94.0
Soda solubility (amount of fiber dissolved at boiling temperature in 7.14 NaOH solution)	Under 10.0
Copper number	Under 2.2
Ash	Under 0.2
Resins	Under 0.25
Pentosans	Under 2.0

The present invention thus makes possible the use of a high alpha cellulose wood fiber, which may be manufactured at a cost materially lower than that at which cotton linters or cotton are available, for the production of high grade nitrocellulose products.

In order to save heat in the production of our mercerized sheet, the tissue may be passed through the strong caustic solution in a moist condition. In this case the caustic solution is preferably made a little stronger than otherwise in order to hasten the penetration of the caustic soda into the sheet. According to this procedure, the beaten or unbeaten sheet is formed in the usual way, passed through squeeze rolls, and then, without being dried, drawn through a caustic soda solution of suitable composition and temperature; or the sheet, if so desired, may be partly dried before it enters the caustic soda solution.

We are, of course, aware of the fact that mercerization of cellulosic material such as cotton is in itself broadly old, but, so far as we are aware, the beneficial and remarkable results obtainable by combining mercerization of a tissue of cellulose fiber of any derivation, and more especially a tissue of mechanically hydrated high alpha cellulose

wood fiber, with nitration have not heretofore been recognized.

The advantages of the process may be extended to the production of other cellulose esters, such for example, as cellulose acetate, for the mercerization of a web of cellulose and more especially high alpha cellulose wood fiber followed by a hot water treatment as hereinbefore described will improve materially the smoothness of acetylation and the quality of cellulose acetate obtained, particularly with regard to the elimination of undesirable color.

From the explanation of the nature of this invention, it is evident that various changes in procedure might be resorted to without departing from its spirit or scope as defined by the appended claims.

What we claim is:—

1. The step in the process of forming cellulose derivatives, which comprises treating a tissue of cellulose fiber with a caustic soda solution of mercerizing strength prior to conversion into such derivatives.

2. A process which comprises treating a tissue of wood fiber with a caustic soda solution of mercerizing strength, and then nitrating such tissue.

3. A process which comprises treating a tissue of wood fiber with a caustic soda solution of mercerizing strength, and then converting such tissue into a cellulose derivative.

4. A process of producing a cellulosic material especially adapted for conversion into cellulose derivatives, which comprises treating a tissue of wood fiber with a caustic soda solution of mercerizing strength, successively washing with hot water, acidifying, again washing the treated tissue, and finally drying the tissue.

5. A process which comprises treating a tissue of wood fiber with a caustic soda solution of mercerizing strength, successively washing, acidifying, and again washing the treated tissue, drying the same, and finally nitrating the dried tissue.

6. A process of producing cellulosic material especially adapted for nitration, which comprises forming beaten wood fiber into thin sheets of tissue suitable for conversion into cellulose derivatives, and mercerizing such tissue.

7. A process which comprises forming beaten wood fiber into thin sheets of tissue, mercerizing such tissue, and nitrating the mercerized tissue.

8. A process which comprises forming wood fiber into thin sheets of tissue, mercerizing such tissue, cutting such tissue into small pieces, and then nitrating such pieces.

9. A tissue especially suitable for conversion into cellulose derivatives, comprising mercerized wood fiber.

10. A tissue especially suitable for conversion into cellulose derivatives, comprising beaten and mercerized wood fiber.

11. A crinkled tissue especially suitable for conversion into cellulose derivatives, comprising a mercerized high alpha cellulose wood fiber.

12. A tissue especially suitable for conversion into cellulose derivatives, comprising a beaten and mercerized high alpha cellulose wood fiber possessing the following characteristics: alpha cellulose content over 94.0%, soda solubility (in 7.14 NaOH) under 10.0%, copper number under 2.2.

13. A process which comprises forming a wet web of cellulosic material, and mercerizing said web before it becomes dry.

14. A process which comprises forming a wet web of cellulosic material, and mercerizing said web for a period under five seconds before it becomes dry.

15. A process which comprises forming a wet web of cellulosic material, mercerzing said web before it becomes dry, drying said web, and then converting it into a cellulose derivative.

16. A tissue especially suitable for conversion into cellulose derivatives, comprising mercerized wood fiber of a basic weight below 20 pounds.

17. A process which comprises treating a tissue of cellulose fiber with a caustic soda solution of mercerizing strength and then treating the mercerized tissue with hot water to remove its caustic soda content.

18. A process which comprises treating a tissue of cellulose fiber with a caustic soda solution of mercerizing strength, treating the mercerized tissue with hot water to remove its caustic soda content, and converting the tissue into a cellulose derivative.

19. A process which comprises treating a tissue of cellulose fiber with a caustic soda solution of mercerizing strength, treating the mercerized tissue with hot water to remove its caustic soda content, and nitrating the tissue.

20. A process which comprises beating wood fiber, sheeting into tissue, mercerizing the tissue, and converting the mercerized tissue into a cellulose derivative.

21. A process which comprises beating wood fiber, sheeting into tissue, mercerizing the tissue, and nitrating the tissue.

In testimony whereof we have affixed our signatures.

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