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MERCERIZED WOOD-FIBER TISSUE AND PROCESS OF PREPARING SAME

No Drawing. Application filed January 5, 1927. Serial No. 159,235.

This invention relates to the preparation of material adapted for conversion into pure or high grade cellulose derivatives, and is more especially concerned with the preparation of cellulosic fiber adapted for conversion into the lower nitrocelluloses, such as those customarily employed for the manufacture of artificial silk, films, lacquers, and kindred products.

Although the process herein to be described may be practised with cellulosic fiber of various kinds, it is applicable most expediently to paper or tissue prepared from wood pulp, particularly one containing a high percentage of alpha or resistant cellulose. Such high alpha cellulose fiber, which for convenience of designation will hereinafter be termed "alpha fiber", may be converted into cellulose derivatives having physical and chemical properties comparable to derivatives 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. Such alpha 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 pulp, e. g., the usual commercial sulphite pulp containing, say, about 85% to 87% alpha cellulose, in a solution of caustic soda or equivalent alkaline compounds under the appropriate conditions of time, temperature, and chemical concentration. By such treatment, a considerable portion of the non-alpha cellulose content of the fiber, viz, beta and gamma celluloses, ligneous and other coloring material, is dissolved, so that there is produced a fiber containing upward of 93% alpha cellulose and which requires only a relatively small amount of bleach for conversion into fiber of high whiteness, and is usable as a new rag or cotton fiber substitute in the manufacture of high grade writing papers and in the preparation of cellulose derivatives of high commercial value and purity. Sometimes it is desirable to treat the pulp, prior to the alkaline treatment, with a halogenizing or an oxidizing solution, e. g., chlorine water, to remove a portion of the non-alpha cellulose constituent or to modify it so as to facilitate its solution by subsequent alkaline treatment, as described in the application hereinbefore mentioned.

When alpha fiber of very high alpha cellulose content, about 95% to 98%, is desired, the initial alkaline treatment is succeeded by a second alkaline treatment, as described in application for patent, Serial No. 75,888, filed December 16, 1925, by George A. Richter. Such double alkaline treatment not only further reduces the quantity of bleach required to whiten the fiber, but produces fiber which constitutes an excellent raw material for the preparation of high grade cellulose derivatives.

In application, Serial No. 140,676, filed October 9, 1926, by George A. Richter, Milton O. Schur, and Royal H. Rasch, the advantages of mercerizing cellulose fiber, and more particularly alpha fiber, prior to conversion into cellulose derivatives, especially the lower nitrocelluloses, are disclosed, and, in our application, Serial No. 140,675, filed October 9, 1926, the advantages of mercerizing paper or tissue formed from such fiber preferably beaten, and a subsequent treatment with hot alkaline water, are disclosed.

We have now discovered that the addition of a relatively small amount of an oxidizing or bleaching agent, e. g., hypochlorite or permanganate, to the mercerizing solution and/or to the hot water, effects an important additional removal of undesirable coloring matter and yields a fiber which is convertible into cellulose derivatives or cellulose products, such as rayon, films, lacquers, etc., of colorlessness or freedom from color practically equal to like derivatives or cellulose products prepared from good cotton fiber.

The use of a small amount of oxidant to remove coloring material from the alpha fiber while such fiber is being treated with a strongly alkaline solution is believed to be distinctly advantageous, for the tremendous OH ion concentration in solution, we believe, represses substantially entirely a tendency toward the oxidation of the alpha or resistant cellulose content of the fiber, while permitting

a selective oxidizing reaction to take place on the non-alpha cellulose content, particularly the coloring matter. This opinion is borne out by the fact that the treatment has substantially no effect upon the excellent nitrating yield, low acid retention, and high strength and stretch of filaments and films prepared from the mercerized fiber. The nitrated fiber may yield solutions of slightly lower viscosity than usual, but this is advantageous for the preparation of many nitrocellulose products.

In carrying out one mode of procedure, the alpha fiber, preferably in tissue form and beaten more or less, is treated by steeping it in a caustic soda solution of mercerizing strength and containing the oxidizing agent, until the desired mercerization of the fiber has been effected. The tissue is then "drowned" or treated with water, preferably hot water, the use of which latter effects a further purification of the fiber. The hot water preserves the tissue in a firm, integral condition, whereas cold water is likely to cause the disintegration of the tissue into a pulpy mass which is difficult to handle. The use of hot water after the mercerizing treatment, as indicated, is therefore a step of paramount importance, as it makes possible the practice of a continuous and economical process. Should the mercerizing solution contain no oxidizing agent, as heretofore, the hot water assumes a deep brown color, the depth of color depending upon the purity or alpha cellulose content of the alpha fiber. When the mercerizing solution contains an oxidizing agent as in accordance with the present invention, however, the hot water is of much lighter color and frequently is colorless, as the tissue retains sufficient oxidant after the mercerizing treatment to oxidize or to bleach coloring matter extracted from or generated in the fiber by the hot, dilute caustic soda solution formed with the hot water. After the hot water treatment, the tissue is neutralized of residual caustic soda by a steeping in an acid or souring solution which preferably contains an acid reducing agent, which, in addition to neutralizing the free caustic soda, neutralizes or reduces the last traces of free oxidant. If desired, of course, a solution containing a mixture of an acid and a reducing compound may be used, but it is usually more expedient to use a single compound to effect both the neutralizing and reducing actions. Thus, for example, sodium hypochlorite may be used as the oxidant in the mercerizing solution, and sulphurous acid may be used in the souring solution as the acid reducing agent. After the souring, the tissue is washed free from neutralized products with cold water, and finally is dried. The tissue tends to crinkle, upon drying, so that if the tension usually applied during drying when the material is in continuous sheet form is reduced or removed, there results a crinkled tissue. Such crinkled tissue may be cut up into small pieces, which when nitrated have but little tendency to stick together in the nitrating bath or in the centrifuge.

A specific example of procedure which may be practised and which has been found to give excellent results, may be substantially as follows. The alpha fiber is preferably treated in the form of a continuous thin waterleaf sheet or nitrating tissue, preferably below 20 pounds in basis weight (480−24×36), or equivalent to a thickness of approximately .003 inches. The fiber is preferably beaten prior to formation into the tissue, as a beaten fiber has proven to give better results upon nitration than an unbeaten fiber. The tissue is passed through or immersed in a caustic soda solution containing about 19% NaOH and about 0.3% available chlorine (based on solution), at about 68° F., the time of immersion being from about two to ten seconds. Under these conditions, we not only realize more effective removal of coloring material and color-generating substances, i. e., substances causing coloration in nitrocellulose products such as lacquers, films, etc., but we retain all the advantages accruing from mercerization. The tissue is then preferably passed between squeeze rolls, which serve to express therefrom excess solution for reuse in mercerization. The tissue is then treated with water, preferably by passing it through a countercurrent flowing stream of hot water at or near the boiling point. The concentrated caustic soda solution retained by the tissue forms with the hot water a dilute caustic soda solution which effects a further removal or extraction of those impurities unaffected by the relatively cold, concentrated mercerizing solution. Since sufficient oxidant is retained by the tissue to bleach any coloring material extracted from or generated in the fiber, the hot alkaline water is light-colored and frequently colorless. The tissue is then passed through a 0.15% to 0.25% sulphurous acid solution at room temperature, and then washed with sufficient cold water to remove the reaction products. The neutral tissue is then dried, either under tension or under conditions permitting it to undergo crinkling, which may be preferable, as the crinkled tissue when cut up into small pieces and nitrated has but little tendency to stick together in the nitrating bath or in the centrifuge.

By our process, two very important ends are simultaneously attained, as in our application hereinbefore identified, viz, the apha fiber is mercerized or chemically hydrated, and it is simultaneously purified or refined. It should be understood that our process is not limited to any specific physical condition of the fiber, but that it might be applied to pulp in bulk or in shredded form, beaten or

unbeaten. With tissue, however, certain practical advantages are to be noted, to wit:

(*a*) Uniformity of treatment is easier to attain, as all the fibers are more easily accessible to the reagents applied.

(*b*) The apparatus necessary is comparatively simple and inexpensive.

(*c*) Continuous operation is more easily realized.

(*d*) The dried, processed tissue, because of its more compact condition, gives a higher yield of nitrocellulose, and has a lower acid retention.

Again, while in the example given certain definite conditions of processing have been specified which have yielded excellent results, nevertheless, we desire to have it understood that the temperature and composition of mercerizing solution, and the time of treatment with such solution, may be varied within rather wide limits.

The tissue may be steeped in the mercerizing solution immediately after sheeting and partial or complete drying, or after sheeting on the wet end of a Fourdrinier or cylinder paper-making machine and passing through press rolls but without drying. A partial or complete conservation of the steam usually expended in drying the tissue may thus be realized, when desired, by the latter method. When a damp or wet tissue is to be mercerized, it is advantageous to employ a stronger solution than otherwise, so as to attain the necessary rate of diffusion into and through the tissue to produce the desired mercerization, but without causing a disintegration or falling apart of the tissue into fragments or into pulp.

If desired, we may also add a very small amount of oxidant to the countercurrent flowing stream of hot water at any suitable point, preferably midway between its influent and effluent ends. Of course, should we so desire, we might omit the addition of oxidant to the mercerizing solution, and add the appropriate amount of oxidant to the countercurrent stream of hot water only. Less oxidant need be added here than to the mercerizing solution, because some of the coloring matter is independently removed by the hot water before the bleaching zone in the countercurrent stream of hot water is reached. The effectiveness of removing coloring material is not lessened, even though the tissue first contacts with effluent colored hot water, because any residual coloring matter in the tissue after mercerization, and/or coloring material ad- or absorbed thereby from the effluent hot water, are gradually removed as the tissue proceeds through the bleaching zone in the countercurrent flowing stream. Such removal of coloring is evidenced by a gradual lightening of the color of the water toward the influent end of the countercurrent stream.

The process of the present invention, by permitting the reduction of the last traces of coloring matter from a mercerized alpha fiber without deleteriously affecting the characteristics which adapt the mercerized fiber for conversion into cellulose derivatives, effects an additional improvement in a wood fiber, which, even heretofore so far as we are aware, is better suited for the production of pure derivatives than any other wood fiber produced. Alpha fiber treated in accordance with the present invention permits the preparation of nitrocellulose and other cellulose derivatives substantially free from coloring matter and from which colorless filaments, films, and congeneric products may be produced. Inasmuch as the absence of coloring matter in nitrocelluloses and other cellulose derivatives prepared from good cotton fiber has in the past been one of the outstanding advantages of cotton as a raw material, and, again, inasmuch as the product of the present invention may be manufactured at a unit cost below that of cotton and its characteristics closely controlled or definitely varied, it is preeminently satisfactory as a pure cellulose raw material.

While the advantages of the present invention have been described in detail in connection with the preparation of nitrocelluloses, and more especially the lower nitrocelluloses, it is to be noted, as previously adverted, that advantages are gained in the preparation of other cellulose derivatives. Thus, in the preparation of cellulose acetate, smoothness of acetylation and quality of cellulose acetate are improved, particularly with regard to the elimination of undesirable color.

We claim:

1. A process which comprises treating a high alpha cellulose fiber with a caustic soda solution of mercerizing strength containing a small amount of an oxidizing agent, substantially completely removing the treating chemicals from the fiber, and converting the fiber into a cellulose derivative.

2. A process which comprises treating a high alpha cellulose wood fiber with a caustic soda solution of mercerizing strength containing an oxidant, washing the treating fiber, neutralizing the last traces of caustic soda and oxidant, and washing the fiber free from reaction products.

3. A process which comprises treating a high-alpha-cellulose-containing wood fiber with a caustic soda solution of mercerizing strength containing a small amount of an oxidant, washing the treated fiber, neutralizing the last traces of caustic soda and oxidant, washing the fiber free from reaction products, and nitrating the fiber.

4. That step which comprises treating a wood fiber web with a caustic soda solution of mercerizing strength containing an oxidant, washing the web substantially free from

treating chemicals, and converting into a cellulose derivative.

5. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidizing agent, and treating the tissue with hot water.

6. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidizing agent, squeezing excess solution from the tissue, and passing the treated tissue through a countercurrent flowing stream of hot water.

7. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidizing agent, passing the treated tissue through a countercurrent flowing stream of hot water, and adding an oxidizing agent to the stream of water.

8. A continuous process which comprises successively passing a continuous sheet of high alpha cellulose fiber through a caustic soda solution of mercerizing strength and through a countercurrent flowing stream of hot water containing an oxidizing agent.

9. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength, passing the treated tissue through a countercurrent flowing stream of hot water, and adding an oxidizing agent to the stream of water.

10. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidant, treating the tissue with hot water, neutralizing caustic soda and oxidant remaining in the tissue, and washing the tissue free from reaction products.

11. A continuous process which comprises successively passing a continuous sheet of high alpha cellulose fiber through a caustic soda solution of mercerizing strength containing an oxidant, through a countercurrent flowing stream of hot water, through a neutralizing solution, and through wash water.

12. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidant, treating the tissue with hot water, neutralizing caustic soda and oxidant remaining in the tissue, washing the tissue free from reaction products, and drying the tissue.

13. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidant, treating the tissue with hot water, neutralizing caustic soda and oxidant remaining in the tissue, washing the tissue free from reaction products, and drying the tissue under conditions permitting it to crinkle.

14. A process which comprises treating a high alpha cellulose wood-fiber tissue with a caustic soda solution of mercerizing strength containing an oxidant, treating the tissue with hot water, neutralizing caustic soda and oxidant remaining in the tissue, washing the tissue free from reaction products, drying the tissue under conditions permitting it to crinkle, and nitrating the crinkled tissue.

15. A process which comprises treating a high alpha cellulose wood-fiber tissue in a caustic soda solution of mercerizing strength containing an oxidant, substantially completely removing the treating chemicals from the tissue, and converting the tissue into a cellulose derivative.

16. A mercerized, high alpha cellulose wood-fiber tissue sufficiently free from non-alpha cellulose components including beta and gamma cellulose, ligneous, and other coloring material to be convertible into lower nitrocelluloses of colorlessness or freedom from color practically equal to nitrocelluloses prepared from good cotton fiber.

17. A process which comprises treating cellulose fiber with a mercerizing solution containing an oxidant, washing the treated fiber substantially free from chemicals, and converting the washed fiber into a cellulose derivative.

18. A process which comprises treating a cellulose fiber tissue with a mercerizing solution containing an oxidant, and washing the tissue substantially free from chemicals in hot water.

19. A process which comprises treating cellulose fiber tissue with a mercerizing solution containing an oxidant, washing the tissue substantially free from chemicals in hot water, and converting the washed tissue into a cellulose derivative.

20. A process which comprises treating a cellulose fiber tissue with a mercerizing solution containing an oxidant, treating the tissue with hot water, drying the tissue under conditions permitting it to crinkle, and converting the crinkled tissue into a cellulose derivative.

In testimony whereof we have affixed our signatures.

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