

UNITED STATES PATENT OFFICE.

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CELLULOSE COMPOSITION FOR ESTERIFICATION AND PROCESS OF PREPARING SAME.

No Drawing.

Application filed March 3, 1927. Serial No. 172,567.

This invention relates to the preparation of a cellulose composition for esterification, being more especially related to the preparation of a composition for nitration, and has for its object the preparation of a composition which when nitrated has a low acid retention and gives a high yield of nitrocellulose.

One process of preparing cellulose fiber for nitration is disclosed and claimed in application, Serial No. 140,677, filed October 9, 1926. In accordance with that process, wood fiber, but more particularly a high alpha cellulose wood fiber, is mercerized prior to nitration. When high alpha cellulose wood fiber is mercerized in bulk form, particularly in the presence of a small quantity of an oxidant, and then nitrated, the resulting nitrocellulose yields solutions of lower viscosity and of markedly better color than those prepared from nitrated, unmercerized fiber.

When mercerized fiber is nitrated in bulk form, however, the acid retention is appreciably higher, and the yield appreciably lower than when unmercerized fiber is first made into thin paper or tissue, which is then mercerized and nitrated as disclosed and claimed in application, Serial No. 140,675, filed October 9, 1926, by Milton O. Schur and Royal H. Rasch. The quality of nitrocellulose obtainable from mercerized bulk fiber, and the physical and mechanical characteristics of filaments, films, lacquers, and kindred products prepared from such nitrocellulose, are, however, apparently as good as when similar fiber in tissue form is nitrated. Apparently, the higher acid retention and lower yield accompanying the nitration of mercerized bulk fiber are imputable to the higher absorptivity of the bulk fiber. Thus, owing to the higher retention of acid by the bulk fiber, a greater loss of the fiber apparently takes place during nitration and when after centrifuging it is submerged in water,—my theory being that the wash water effects a slower dilution and washing out of the acid in the bulk fiber than when tissue is washed, and that during such slower dilution acid concentrations are produced in the bulk fiber, which favor a hydrolysis of nitrocellulose. If, however, it is attempted to form thin paper from the

mercerized fiber, it is found that because mercerized fiber remains practically unhydrated, even when it is beaten several times as long as that required for unmercerized fiber, a bulky, loosely felted paper, which upon nitration shows practically no improvement over bulk mercerized fiber, is produced. This difficulty may be overcome, as disclosed in my application, Serial No. 172,568, filed March 3, 1927, by admixing unmercerized fiber, preferably in beaten condition, with the mercerized fiber.

The object of the present invention is to produce a relatively strong, dense paper or tissue from mercerized cellulose fiber without the use of unmercerized fiber, whereby the desiderata of lower acid retention and higher yield may be realized. I have found that this object may be attained by treating the mercerized fiber with a solution of nitrocellulose or with a cellulose derivative capable of being regenerated into cellulose, and then, if other than nitrocellulose be employed, regenerating the cellulose in situ on the fiber. For instance, a mercerized fiber paper may be formed, then passed through a solution of cellulose xanthate, and the cellulose regenerated in situ in the paper. The fibers thus become encased in and bonded together by regenerated cellulose, which serves to increase the strength and density of the paper. When a paper thus permeated with regenerated cellulose is nitrated, it is found that the acid retention is appreciably lower, and the nitrocellulose yield appreciably higher than when mercerized bulk pulp is nitrated.

The production of a mercerized fiber paper permeated with regenerated cellulose may be accomplished by several different procedures. Thus, one method of procedure may be substantially as follows. Mercerized cellulose fiber is run out on a paper machine into thin sheets or tissue. The paper thus formed is loose and bulky, but these characteristics may be made less pronounced by incorporating a small proportion of unmercerized fiber, either beaten or unbeaten but preferably the latter, into the mercerized fiber. The paper is then saturated with a cellulose xanthate solution of sufficient cellulose con-

centration to yield about 2% to 5% regenerated cellulose, when regenerated in the paper. The paper is then partially or completely dried and immersed in a cellulose-regenerating reagent, e. g., a solution of sodium bisulphate and sulphuric acid, to effect a regeneration of cellulose in situ in the paper. The paper may then be washed, steeped, if desired, in a sulphur-removing reagent, e. g., a sodium sulphide solution, again washed, and finally dried. Preferably, the dry paper is calendered and/or supercalendered, as this compacts it and further enhances its suitability for nitration. The percentage of regenerated cellulose incorporated into the paper may vary, but the treatment is in any case performed so as to effect the encasement and bonding together of the fibers with regenerated cellulose.

Another method of incorporating regenerated cellulose into the paper may be performed similarly to beater-sizing. In such case, cellulose xanthate solution is added to the mercerized fiber in the beater engine, and after it has been uniformly disseminated throughout the pulp, a regenerating reagent is added. The pulp may then be washed and run out on a paper machine into thin paper, which is dried and preferably calendered.

The cellulose may also be regenerated from cellulose derivatives other than viscose. For instance, the regeneration of cellulose may occur from other esters or from cuprammonium cellulose, but cellulose xanthate is preferred, because it is less expensive and easier to treat successfully. When nitro-cellulose is employed as the cellulose derivative, its regeneration into cellulose need not be effected, as no acid grouping which might affect nitration or the quality of the nitrocellulose is present in the paper. In such case, the mercerized fiber is treated with a solution of cellulose nitrate in an ether-alcohol mixture, for example, and the solvent then evaporated and recovered, thus leaving the fibers encased and bonded together with cellulose nitrate, which serves to strengthen and densify the paper. The paper is then preferably calendered, as previously. Where, however, it is undesirable to allow nitrocellulose to remain in the paper, as for instance where such paper is to be stored or shipped, the nitro-cellulose may be regenerated into cellulose as is effected when cellulose derivatives other than nitrocellulose are employed. This may be accomplished, for example, by steeping the paper in a denitrating bath, e. g., a sodium sulphide solution, whereupon the paper may be washed and dried.

While fiber made into paper gives the best results upon nitration, nevertheless bulk mercerized fiber which has been treated with regenerated cellulose or nitrocellulose when nitrated in bulk form gives improved results over bulk mercerized fiber alone. For in-

stance, bulk mercerized fiber which has been treated with regenerated cellulose or nitro-cellulose may be fluffed mechanically to resemble cotton linters, or may be formed as a relatively thick, loosely felted, uncompacted web on a Fourdrinier wire or a cylinder machine, and nitrated in such form.

In any of the procedures hereinbefore given, the mercerized fiber has been prepared for nitration without the introduction of foreign materials which would be nitrated along with the cellulose and contaminate the nitro-cellulose.

The utility of the process herein described is that the advantage of mercerizing fiber in bulk form, as well as the advantage arising from a desirable physical condition of fiber when nitration is being effected, are both realized. In plant practice, it is more economical to mercerize and wash pulp in large quantities in bulk form and to recover the mercerizing solution, rather than to mercerize thin paper or tissue. By the process of the present invention, the economical advantages of mercerizing fiber in bulk form are enjoyed, and at the same time a paper of good nitrating characteristics may be manufactured therefrom.

Having thus described certain embodiments of this invention, it is obvious that these may be varied without departing from the spirit or scope of invention as set forth in the appended claims.

What I claim is:

1. A composition comprising mercerized cellulose fiber and regenerated cellulose deposited on said fiber.
2. A composition comprising mercerized cellulose fiber and a cellulose derivative deposited on said fiber.
3. A paper comprising mercerized cellulose fiber permeated with regenerated cellulose.
4. A paper comprising mercerized cellulose fiber permeated with a cellulose derivative.
5. A calendered paper comprising mercerized cellulose fiber permeated with regenerated cellulose.
6. A process which comprises running mercerized fiber out on a paper machine, and permeating the paper with a cellulose derivative.
7. A process which comprises running mercerized fiber out on a paper machine, permeating the paper with a cellulose derivative, and regenerating cellulose in situ in the paper.
8. A process which comprises running mercerized fiber out on a paper machine, permeating the paper with a cellulose derivative, regenerating cellulose in situ in the paper, and calendering the paper.
9. A process which comprises running mercerized fiber out on a paper machine, per-

meating the paper with a cellulose derivative, regenerating cellulose in situ in the paper, and nitrating the paper.

5 10. A process which comprises running mercerized fiber out on a paper machine, saturating the paper with a solution of cellulose xanthate, drying the paper, regenerating cellulose in situ in the paper, and nitrating the paper.

10 11. A process step which comprises permeating paper composed of mercerized cellulose fiber, with a cellulose derivative.

15 12. A process which comprises permeating paper composed of mercerized cellulose fiber, with a cellulose derivative; and nitrating the same.

13. The process step which comprises permeating paper composed of mercerized cellulose fiber, with regenerated cellulose.

20 14. A process which comprises permeating

paper composed of mercerized cellulose fiber, with regenerated cellulose; and nitrating the same.

15. A process which comprises fixing regenerated cellulose on mercerized cellulose fiber, and then running the fiber out on a paper machine. 25

16. A process which comprises fixing regenerated cellulose on mercerized cellulose fiber, running the fiber out on a paper machine, and nitrating the paper. 30

17. A process which comprises incorporating a solution of cellulose xanthate into mercerized cellulose fiber, adding a regenerating reagent to the fiber, thereby regenerating cellulose on the fiber; and running the fiber out on a paper machine. 35

In testimony whereof I affixed my signature.

GEORGE A. RICHTER.