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ACTIVATION OF CELLULOSE FOR CONVERSION INTO CELLULOSE DERIVATIVES

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This invention relates to the activation of cellulose designed to undergo conversion into cellulose derivatives. While not restricted thereto, it is more particularly concerned with putting cellulose in a condition such that it can be acetylated to best advantage.

In making cellulose derivatives and more particularly cellulose acetate, it is found that the smoothness and rate of reaction may vary greatly, depending upon the source, chemical purity, and physical condition of the cellulose used as raw material. The quality of the resulting cellulose derivative is also a reflection of the kind of cellulose serving as the starting material. Some kinds of cellulose are found to be notably resistant to the usual acetylating mixture in the sense that they do not become uniformly and completely acetylated or do not enter into chemical combination at a suitable rate. Unfortunately, this is especially true when the cellulose has undergone treatment with alkaline liquors which may effect a highly desirable chemical purification of the cellulose. For instance, chemical wood pulps, cotton, or other forms of cellulose which have been rid of considerable, if not mostly all, of their non-alpha cellulose constituents by treatment with strongly alkaline liquors are apt to acquire a more or less passive state toward acetylating mixtures. Indeed, the stronger the alkaline purifying liquor, the more passive is the cellulose apt to become toward acetylating mixtures. Thus, in the case of cellulose which has undergone the action of a liquor of mercerizing activity, the fiber may become so passive as to be virtually non-acetylatable. Yet, from a chemical standpoint, the subjection of cellulose to a mercerizing liquor may be highly worthwhile in the sense that such a liquor is capable of bringing about a refinement of the cellulose, such as raising the alpha cellulose content (about 87% to 89%) of the ordinary wood pulps to about 94% to 96% or even higher or dissolving the waxy or similar impurities associated with cotton.

We have discovered that by treating cellulose with an aqueous solution of a water-miscible liquid, polyhydric alcohol, it is possible to effect a marked activation of the cellulose for conversion into cellulose derivatives and more especially for conversion into cellulose acetate. Indeed, we have found that by performing such preliminary treatment upon mercerized cellulose which does not acetylate at all properly, it is possible to realize cellulose activated to such a degree as to be satisfactorily acetylatable. In ap-

plying the principles of our invention, all that we need do is to wet the mercerized cellulose uniformly with an aqueous solution of polyhydric alcohol, e. g., glycerine, remove the water, as by evaporation, and then proceed to acetylate the cellulose as ordinarily.

While we cannot account with precision for the result which we secure, nevertheless we have formulated a theory which appears to be a logical one in view of such facts as we have been able to muster at this time. Taking mercerized cellulose fiber as an example, microscopic examination indicates rather strongly that mercerization has shrunk its structure and increased its density. We suspect that this physical change in fiber structure is responsible for the poorly acetylatable qualities of mercerized fiber. When mercerized fiber is wetted with plain water, it evidently undergoes expansion, but this expanded state is evidently lost when the fiber is dried. When, on the other hand, an aqueous solution of glycerine, ethylene glycol, or similar liquid polyhydric alcohol, which has a much higher boiling point than water, is applied to the fiber and the water is evaporated, it appears that the residuum of polyhydric alcohol remaining on the fiber inhibits a shrinkage of the fiber to its original density, wherefore, the fiber is in a physical condition amenable to satisfactory combination with the acetylating mixture. Whether or not our theory is correct, it is a fact that by practicing the treatment hereinbefore outlined, it is possible to arrive at the desired activated state in mercerized fiber and to improve for acetylation and for conversion into other cellulose derivatives, semi-mercerized fiber, fiber which has undergone the refining action of a non-mercerizing alkaline liquor, and other kinds of fiber such as cotton, pulped cotton rags or linen rags, pulped softwoods or hardwoods, hemp, etc.

A specific example of procedure practiced accordant with the present invention may involve starting with chemical wood pulp, such as sulphite, as raw material. Such wood pulp in bulk or sheet form may be subjected to the action of an alkaline refining liquor, say, of mercerizing or of semi-mercerizing activity, until its alpha cellulose content has been increased to about 94% to 96% or even higher. Caustic soda solution of, say, about 10% to 18% or greater strength may serve as the refining liquor for this purpose at room or at below room temperature. In some case, the refinement may be carried out at room temperature in caustic soda solution of, say, 6% to 10% strength, or at elevated

temperature in more dilute caustic soda or other alkaline solutions. In some cases, a suitable reducing agent such as sodium sulphide, may be included in the alkaline liquor. In other cases, it may be desirable to add a suitable oxidant such as sodium hypochlorite, peroxide, or permanganate to the alkaline liquor to improve the whiteness of the fiber or to impart thereto the quality of low solution viscosity. This latter quality may be desired as, for instance, when the cellulose acetate is to enter into lacquer compositions which should be possessed of low viscosity. In some instances, not only may the fiber undergo the action of a mercerizing liquor containing an oxidant to promote the lowering of the solution viscosity of the fiber, but the liquor-treated fiber may, after the removal of excess solution therefrom, be aged until it acquires the desired low solution viscosity. Indeed, the fiber treated with a mercerizing liquor containing merely caustic soda may undergo ageing, such as is currently practiced in the viscose-making industry, to acquire a low solution viscosity. The alkaline liquor may then be washed from the refined fiber which may first be dried or treated without intermediate drying with an aqueous solution of polyhydric alcohol. To this end, we prefer to use a glycerine solution of moderate strength, say, one of 10% to 15% glycerine concentration. Assuming that bulk fiber is thus being glycerinated, the fiber may be suspended as a pulp in the aqueous glycerine solution so as to ensure substantially uniform wetting of the fiber and the suspension then delivered into a centrifuge or to any other device capable of extracting free or unabsorbed liquid. The partially deliquesced cellulose mass is then substantially completely dehydrated as in an atmosphere heated to about 100° C. The strength of the aqueous glycerine solution and/or the degree to which mechanical extraction of the solution-treated fiber is effected may be controlled to yield a substantially dehydrated fiber containing about 5% to 20% of glycerine, based on the dry weight of fiber, distributed substantially uniformly therethroughout. It is desirable to avoid leaving a greater residue of glycerine in the fiber even though the glycerine may, in some cases, be non-injurious or, in fact, beneficial to the acetylated product, since it is consumptive of the acetic acid and acetic anhydride used in the acetylating mixture. The glycerinated but substantially dehydrated fiber may be acetylated in the usual manner and the resulting cellulose acetate put through the usual after-treatments designed to yield a finished acetone-soluble product. Not only does acetylation proceed smoothly at the desired rate, but the finished cellulose acetate dissolves substantially completely in acetone to form solutions or lacquers characterized by their excellent clarity and substantial freedom from color.

It is possible to use ethylene glycol or other glycols or liquid polyhydric alcohols for the purposes of our invention, but glycerine is the most attractive polyhydric alcohol both on account of its comparatively low cost and the excellent results producible thereby. It is to be noted, however, that the desired results are not realized by applying glycerine or its equivalent in anhydrous condition to the dry fiber. In other words, it is evidently the swelling or expanding action exercised by the water on the fiber, coupled with the shrinkage-inhibiting effect of the glycerine on the fiber when the water is removed there-

from, that gives rise to the desired activated condition in the fiber. The fact is that the use of a concentrated glycerine solution, say, one of 80% strength in treating the fiber does not conduce to results as good as those had with the weaker glycerine solutions cited in our specific example.

In some cases, it may be desirable to remove the glycerine residuum associated with the dehydrated fiber before the fiber is subjected to acetylation. In such case, the extraction should be effected in such a way as to avoid rehydration of the fiber. For instance, dehydrated glycerine-containing fiber may be extracted with anhydrous alcohol or other volatile anhydrous solvent for the glycerine. Such a procedure can be practiced with a recovery of substantially all the glycerine and solvent. The distillation of the glycerine under vacuum from the fiber, although possible, is not as easy to effect as in the case of ethylene glycol which has a higher vapor pressure curve and is of somewhat lower boiling point. A super-heated steam-distillation of the glycerine from the fiber, as contrasted with a wet-steam distillation, presents another possible way of removing the glycerine or other polyhydric alcohol from the fiber without substantially re-wetting or rehydrating it.

The principles of the present invention may be applied advantageously to cellulose in powdered as well as in fibrous form. Thus, we have found that even a normal or unmercerized cellulose which has been reduced to pulverulent condition in a ball mill or similar impact machine in the absence of water does not acetylate as well as does the fiber before subjection to the action of the ball mill. In some cases, the acetylatability of the cellulose is largely destroyed through the action of a ball mill thereupon. We believe that this change in behavior of the cellulose is attributable to the increased density of the cellulose particles arising from the pounding action relied upon to smash the fiber wall into bits. We have demonstrated that the wetting of the cellulose powder thus attained with an aqueous glycerine solution or similar polyhydric alcohol solution and the dehydration of the cellulose particles, as hereinbefore described, results in a cellulose that acetylates quite readily. When the same sort of treatment is performed on a mechanically pulverized cellulose prepared from mercerized cellulose fiber, it is found that such powder also behaves much better upon acetylation. In speaking about powdered cellulose, we mean cellulose fiber which has been reduced in ball mills, roller mills, stamp mills, kollergangs, or similar impact machines, to a particle size of, say, 40 to 200 mesh or even finer. After the cellulose powder has been treated with the aqueous glycerine solution and then dehydrated as already described, it may be sifted through a sieve of suitably fine mesh to eliminate such lumps as may have developed therein; and its glycerine content may, if desired, be extracted or removed therefrom substantially without causing rehydration by such treatments as have hereinbefore been described.

While we have stressed the importance of our discoveries in connection with the preparation of cellulose acetate, it is to be understood that there is no intention on our part to limit our invention to the preparation of this cellulose derivative alone. As will be understood by those skilled in the art, it may be desirable in preparing various other derivatives or compounds of cellulose in-

cluding such esters as cellulose nitrate, cellulose xanthate, cellulose formate, etc., and such ethers as ethyl or methyl cellulose, to expose the cellulose in an uncompacted or unshrunk condition and presenting as much surface area as possible to the esterifying, etherifying, or other converting reagent. In such case, one may advantageously practice treatments similar to those hereinbefore described as putting cellulose in an improved condition for acetylation. Other than containing glycerine or other polyhydric alcohol which, too, may be removed if desired as hereinbefore described from cellulose activated in accordance with my invention, the cellulose so activated is substantially devoid of non-cellulosic ingredients which would be consumptive of acetylating chemicals or other converting reagent.

We claim:—

1. A process which comprises refining cellulose in alkaline liquor, associating the resulting cellulose with an aqueous solution of glycerine, dehydrating the cellulose, and acetylating it.

2. A process which comprises associating mercerized cellulose with an aqueous glycerine solution, dehydrating the mercerized cellulose, and acetylating it.

3. A process which comprises refining cellulose in an alkaline liquor, associating the refined cellulose with a solution of a polyhydric alcohol of a strength not greater than about 10% to 15%, dehydrating the cellulose, and converting the cellulose into cellulose compounds.

4. A process which comprises refining cellulose in a mercerizing alkaline liquor, associating the refined mercerized cellulose with a glycerine so-

lution of a strength not greater than about 10% to 15%, dehydrating the cellulose, and converting the cellulose into cellulose compounds.

5. A process which comprises refining cellulose in a mercerizing alkaline liquor, associating the refined mercerized cellulose with a glycerine solution of a strength not greater than about 10% to 15%, dehydrating the cellulose, and acetylating it.

6. A process which comprises refining cellulose in an alkaline liquor, associating the resulting cellulose with an aqueous solution of polyhydric alcohol, dehydrating the cellulose, and converting the cellulose into cellulose compounds.

7. A process which comprises refining cellulose in an alkaline liquor, associating the resulting cellulose with an aqueous solution of polyhydric alcohol, dehydrating the cellulose, and acetylating the cellulose.

8. A process which comprises refining cellulose in an alkaline liquor of mercerizing activity, associating the refined mercerized cellulose with a solution of a polyhydric alcohol of a strength not greater than about 10% to 15%, dehydrating the cellulose, and converting the cellulose into cellulose compounds.

9. A process which comprises refining cellulose in an alkaline liquor of mercerizing activity, associating the refined mercerized cellulose with a solution of a polyhydric alcohol of a strength not greater than about 10% to 15%, dehydrating the cellulose, and acetylating the cellulose.

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