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TREATMENT OF PULP

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This invention relates to wood pulp, especially to mercerized high-alpha wood pulp to be used for acetylation. The invention is more particularly concerned with the activation of a mercerized, high-alpha wood pulp toward acetylating agents, and provides an improved method of activation which involves the attrition of such a pulp in the presence of acetic acid.

The invention provides a method for the activation of high-alpha mercerized wood pulps so that they may be acetylated satisfactorily by the present industrial procedures which comprises grinding the mercerized wood pulp in contact with concentrated acetic acid before subjecting it to any one of the usual acetylation procedures.

The wood pulps generally used at present by the manufacturers of cellulose acetate are prepared by a hot-caustic refining process; i. e., the previously liberated fiber is cooked in a caustic soda solution at a temperature of at least 100° C. after which it is bleached, dried on a paper machine and supplied to the industry in the form of bales of sheets or rolls. Such pulps, which have a maximum alpha-cellulose content of approximately 96%, may be acetylated by any of the usual commercial processes to give a highly satisfactory product, particularly if the sheets have been mechanically separated into individual fibers in the presence of glacial acetic acid according to the process disclosed in our United States Letters Patent 2,415,949.

When wood pulp is extracted with caustic soda solutions of concentrations higher than 5% and at temperatures below 100° C., and subsequently washed and dried, it is found to be partially or entirely inactive toward acetylation or other organic esterification, even if the drying operation has been carried out at temperatures as low as 25° C. Furthermore, such a pulp cannot be completely acetylated by the usual methods even if the esterification operation be prolonged far beyond the point of commercial practicability or carried out at such a high temperature that undue reduction in viscosity and discoloration of the product take place. This inactivity, which is augmented as the caustic soda solution temperature is lowered or its concentration increased, is presumably due to total or partial mercerization of the cellulose. The marked changes which take place in the physical and chemical properties of cellulose as a result of mercerization are thought to be due to changes in the lattice structure of the crystallites, to a decrease in the degree of orientation of the crystallites, or to an increase in the ratio of amorphous to crystalline material.

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Inactivation of the pulp takes place to a marked degree when the caustic extraction is carried out below 35° C., even though the NaOH solution concentration be substantially lower than 10%. At NaOH concentrations above 12%, considerable inactivation occurs even when the extraction temperature is as high as 70° C. When caustic soda solutions of 12% or higher concentrations are used, the alpha-cellulose content of the resulting pulp may rise to a value as high as 98.5% or 99%. Such a pulp, when acetylated under the proper conditions, is capable of yielding a product which has a color and clarity fully equal to that of cellulose acetate prepared from cotton linters. However, this type of pulp has not been used to any appreciable extent in the industrial production of cellulose acetate because of its extreme inactivity toward the acetylating agents. Although many procedures have been proposed for avoiding or overcoming this inactivity, none has thus far proved to be commercially feasible. For example, the mercerized pulp after mechanical disintegration may be subjected to a prolonged pretreatment with from 15% to 50% of its weight of glacial acetic acid prior to acetylation. Another procedure involves removing the water from undried mercerized pulp by repeated extractions with glacial acetic acid before carrying out the acetylation proper.

Mercerized wood pulp, even when dried in the air at ordinary temperatures, i. e., 20° C. to 30° C., is substantially inactive toward acetylation. This inactivity is increased to a marked extent as the drying temperature is increased. For example, a sulfite pulp which has been extracted with a 12% NaOH solution at a temperature of 25° C., washed, and subsequently dried in sheet form at a moderately elevated temperature such as 60° C., is extremely inactive toward acetylation. The inactivity of such a sample cannot be overcome even when the sheet is mechanically disintegrated into the individual fibers in the presence of glacial acetic acid according to the process disclosed in our said Patent 2,415,949. A pulp of this type is even more inactive when dried on a commercial paper machine where still higher temperatures prevail.

We have discovered that mercerized high-alpha pulps which have been dried at elevated temperatures may be rendered practically completely active toward acetylation by subjecting them to attrition in the presence of glacial acetic acid. As pointed out in the previous paragraph, the activation is not effected merely by disintegrating the sheet into a loose, fibrous form, but the mixture of pulp and acetic acid must be ground and kneaded in such manner that the in-

dividual fibers are cut and split in addition to being ruptured and fibrillated by a mutual vigorous rubbing action.

One kind of equipment which has proved to be suitable for the grinding operation is a Baker-Perkins shredder of the type commonly used by the viscose rayon industry for shredding alkali-cellulose prior to xanthation. In such a shredder the fibers of cellulose, moistened with acetic acid, are vigorously ground and rubbed between the serrated edges of the S-shaped mixing or kneading arms and the sharply knurled surfaces of the saddle bar. Any type of shredder which exerts the grinding, kneading and rubbing action (for convenience herein called "grinding") described above would be suitable for carrying out this operation. In practice, the shredder or grinder would most conveniently be located immediately above the acetylator, so that the mass of shredded pulp and acetic acid could be discharged directly through a chute, thus preventing the escape of acid fumes into the air.

The ratio of pulp to acetic acid during the grinding operation may vary over a wide range, depending upon the type of equipment used. However, we prefer to operate between consistencies of 20% and 40% when using the shredder described above. The term "consistency" refers to the percentage of the pulp present in the mixture of pulp and acetic acid. The acetic acid used may be anhydrous, or may contain as much as 5% to 10% water. However, for a minimum consumption of acetic anhydride in the subsequent acetylation, the water content of the acid should be as low as practicable. The moisture content of the pulp is not critical, but here again, economic factors dictate that the pulp be as dry as possible. We prefer to operate in the range 2.5% to 6% moisture. The temperature at which the grinding operation is carried out may range from the freezing point to the boiling point of acetic acid. For practical purposes, however, we prefer to operate at temperatures between 20° C. and 60° C. The duration of the grinding operation may vary from 30 minutes to five or six hours, the preferred range being from one to two hours. In starting the operation, the sheeted wood pulp, previously cut or torn into coarse pieces by any suitable type mechanical disintegration, may be charged into the grinding equipment along with the proper amount of acetic acid. Other optional procedures would involve spraying the sheeted pulp with the proper amount of acetic acid or passing it over a roll which dips into an acetic acid bath or passing the sheet through the acid bath itself before feeding it into the grinder.

The following experiments were carried out in order to demonstrate that the mere presence of acetic acid in contact with the pulp is not sufficient for the activation, but that the concurrent grinding and rubbing action is necessary. The experiments also show the effects quantitatively.

SERIES I

Experiment 1.—A 200-gram sheet of a hemlock sulfite pulp which had been extracted with 12% NaOH solution at 25° C., bleached, and dried in the air at 23° C. was torn into pieces of approximately one square inch area and then ground in a Baker-Perkins laboratory-size alkali-cellulose shredder in the presence of 400 cubic centimeters of glacial acetic acid for one hour at a temperature of 20° C. A portion of the resulting crumb-like material was then acetylated by a standard method without further pretreatment. At the end of the normal acetylation cycle a clear, nearly colorless gum was obtained which contained only a comparatively small quantity of unreacted fiber. The percentage of this unreacted material (based upon the weight of original pulp) was determined by allowing the triacetate gum to stand until the portion which did acetylate had attained acetone solubility, after which a weighed aliquot portion of the thoroughly agitated gum was diluted with acetone and poured through a sintered-glass funnel. The unreacted fibers were then washed with acetone, dried and weighed.

Experiment 2.—This was a control for the previous experiment. A 25-gram portion of the same pulp tested in Experiment 1 was carded by hand into a loose, fibrous form and immersed in 350 cubic centimeters of glacial acetic acid after which the mixture was allowed to stand for one hour at a temperature of 20° C. The excess acid was then pressed out in a Büchner funnel and the residue subjected to acetylation by a standard method without further pretreatment. The percentage of unreacted fibers was determined in the same manner as described under Experiment 1.

The results of these two experiments are shown in Table I.

Table I

Expt. No.	Unreacted Fibers
	Per Cent
1	0.51
2	39.4

SERIES II

Another series of experiments was carried out on a similar pulp which, however, had been dried in an oven at 105° C. to a 94.0% bone-dry content and then allowed to cool in the air to room temperature.

Experiment 3.—A 200-gram sheet of the pulp was torn into pieces of approximately one square inch area and ground in the shredder with 400 cubic centimeters of glacial acetic acid for two hours at a temperature of 25° C. A portion of the resulting crumb was then acetylated without further pretreatment.

Experiment 4.—This was carried out in the same manner as the previous experiment except that the duration of the grinding operation was only one hour.

Experiment 5.—This experiment was a control for the series. A 25-gram portion of the pulp which had been carded by hand was treated with 275 cubic centimeters of glacial acetic acid and the mixture allowed to stand for one hour at a temperature of 25° C. The excess acid was then pressed out on a Büchner funnel after which the pulp was acetylated without further pretreatment.

In each case, the percentage of unreacted fibers was determined as previously described. The results are shown in Table II.

Table II

Expt. No.	Unreacted Fibers
	Per Cent
3	0.085
4	0.84
5	71.9

It is evident from the results of the foregoing experiments that grinding and rubbing mercerized wood pulp in the presence of acetic acid overcomes the inactivity brought about by mercerization and also the additional inactivity caused by drying the pulp at elevated temperatures. It is also evident that the same beneficial results cannot be brought about by merely steeping the pulp in acetic acid under similar conditions of time and temperature.

The advantages of the process of this invention over those previously disclosed are at once apparent. Although the method which involves pretreating the mechanically disintegrated pulp with from 15% to 50% of its weight of glacial acetic acid is reasonably effective in overcoming the inactivity due to machine drying and to mechanical disintegration, we have found that periods of pretreatment as long as 24 hours or more may be necessary to overcome completely the inactivity due to mercerization. From an industrial standpoint, this pretreatment is undesirable for many reasons, chief of which is the necessity of providing a large volume of acid-proof storage space for the prolonged operation. The alternative procedure often proposed, in which mercerized pulp containing at least 25% moisture is dried by successive extractions with glacial acetic acid is commercially impractical for at least two reasons. In the first place it is necessary to concentrate huge volumes of diluted acetic acid by means of costly fractional distillation equipment. In addition to this disadvantage, the method involves the transportation of substantial tonnages of useless water over the hundreds or even thousands of miles that separate the pulp mills from the acetylating plants. In sharp contrast to these procedures, which at best are slow, cumbersome and costly, the method of the present invention is rapid, direct and convenient.

The method of this invention may be used in esterification generally as, for example, in the production of cellulose acetate propionate and cellulose acetate butyrate. These compounds may be produced as mixed esters by introducing propionic acid and/or propionic anhydride, or butyric acid and/or butyric anhydride, as the case may be, into the esterification mixture which contains, in addition, acetic acid, acetic anhydride and sulfuric acid. The method of the present invention may be applied to the preparation of these compounds by grinding the mercerized wood pulp with either acetic acid, a mixture of acetic and propionic or butyric acids, or propionic or butyric acid alone.

We claim:

1. In the treatment of high-alpha mercerized wood pulp to render it active toward acetylation resulting in a lower percentage of unreacted fibers, the improvement which comprises grinding the mercerized wood pulp dried to a moisture content of not over 6% in contact with the acetic acid.

2. In the treatment of high-alpha mercerized wood pulp to render it active towards acetylation resulting in a low percentage of unreacted fibers, the improvement which comprises charging simultaneously into a grinding operation the wood pulp and glacial acetic acid and grinding the mercerized wood pulp in contact with the acetic acid to render the pulp active toward acetylation.

3. In the treatment of high-alpha mercerized wood pulp for acetylation, the improvement which comprises impregnating mercerized wood pulp containing a low amount of water, not over 6% by weight, with acetic acid containing not over 10% of water, and grinding the pulp immediately after impregnating with acetic acid to cut and split the fibers and render it active toward acetylation.

4. In the treatment of high-alpha-mercerized wood pulp for acetylation, the improvement which comprises impregnating mercerized wood pulp containing a low amount of water, not over 6% by weight, with acetic acid containing not over 10% of water in an amount giving a consistency of from 20% to 40% and grinding the pulp immediately after impregnating with acetic acid to cut and split the fibers and render it active toward acetylation.

5. In the method of claim 4, carrying out the grinding for a period of from one-half to six hours.

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