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TREATMENT OF WOOD

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This invention relates to the treatment of wood, and relates more particularly to the production of organic esters of cellulose of relatively high degree of esterification from organic esters of cellulose of relatively low degree of esterification prepared by digesting wood particles with a lower aliphatic acid.

An object of this invention is the provision of an improved process of preparing organic esters of cellulose of relatively high degree of esterification and of satisfactory clarity and color in a rapid, efficient and economical manner.

Another object of this invention is to provide an improved process for preparing organic esters of cellulose of relatively high degree of esterification by further esterifying organic esters of cellulose of relatively low degree of esterification produced by digesting wood particles with a lower aliphatic acid and then treating the cellulose pulp under such conditions that the acyl groups attached thereto during the digesting step are not removed.

Other objects of this invention will appear from the following detailed description.

Processes for making organic esters of cellulose from wood pulp have heretofore yielded products which were not wholly satisfactory from the standpoint of clarity and color.

We have now discovered that wood pulp eminently satisfactory for use in the production of organic esters of cellulose of high clarity and good color may be obtained by digesting wood particles in the presence of a lower aliphatic acid. In accordance with our invention, wood in a particle form, for example, sawdust, is first cooked or digested with acetic acid or other lower aliphatic acid under elevated temperature and pressure. After cooking, the pulp is boiled with acetic acid, and is then subjected to a series of washing operations with progressively weaker acid, and is finally washed neutral with water. The neutral pulp may then be chlorinated, bleached and dried.

The partly esterified wood pulp produced by our process is not only of greatly increased purity but, in addition, has a substantial number of acyl groups combined therewith. When this partially esterified wood pulp is subjected to further esterification to convert the same into cellulose esters of higher degree of esterification, this partly esterified cellulose requires the use of less aliphatic acid anhydride to reach the desired higher degree of esterification. Moreover, the present process permits of careful temperature control during said esterification reaction and, accordingly, only a limited amount of cooling is necessary to maintain the temperature of the exothermic esterification reaction within the desired limits. Since the temperature may be maintained under precise control with little refrigeration, the process is very economical and the cellulose ester obtained upon esterifying the cellulose ester of relatively low degree of esterification is of excellent characteristics.

In accordance with our process, the acetic acid or other lower aliphatic acid employed in cooking the wood may be of varying concentrations. Thus, for example, aqueous solutions containing about 85% of the acid, or less, may be employed. However, more concentrated acids, viz. glacial acetic acid, are preferable. The temperature in the digester may be from 130 to 220° C. and the time of the treatment may vary from 1 to 10 hours. By digesting the wood with acids and then further treating the pulp obtained in accordance with our invention, the acid may not only be combined with the cellulose to the extent of 5 to 18% by weight (calculated as the corresponding acid) but the additional treatment removes little or none of the combined acid. As a result, the partially esterified cellulose treated in accordance with our process, namely, chlorinating, bleaching and drying the same, forms an excellent starting material for further esterification in the production of cellulose acetate or other organic esters of cellulose.

In chlorinating the partially esterified wood pulp, chlorine is employed in excess and the excess may vary from 1 to 10% on the weight of the pulp treated. Usually, a chlorination treatment for from 30 to 60 minutes is sufficient, but optimum results are achieved when the chlorination is permitted to proceed for about 30 minutes with about 2% of excess chlorine.

The bleaching of the partially esterified wood pulp is preferably carried out employing sodium hypochlorite but sodium chlorite, potassium permanganate or hydrogen peroxide may also be employed. When sodium hypochlorite is employed, the solution may contain from ½ to 3% of available chlorine and a satisfactory bleach obtained in from 1 to 3 hours with the solution at from 20 to 50° C. We have found that with about 1% of available chlorine present, optimum results are obtained in 3 hours at 35° C.

In order further to illustrate our invention but without being limited thereto, the following example is given:

Example

Twenty parts by weight of oven-dry black spruce sawdust are digested in a suitable digester with 125 parts by weight of glacial acetic acid for 5 hours at 180° C. under autogenous pressure.

When the digestion is completed the pulp is boiled twice with glacial acetic acid and is then washed neutral with hot water after being given several washes with progressively weaker acetic acid. After being washed neutral, the wood pulp is subjected to chlorination for 30 minutes with 10% excess chlorine, and following chlorination, the pulp is bleached for 3 hours at 35° C. in sodium hypochlorite with 1% of available chlorine present. The pulp obtained by this treatment has an acetyl value of 15%, calculated as acetic acid.

An acetylation mixture comprising 319 parts by weight of acetic anhydride, 656 parts by weight of acetic acid and 25 parts by weight of sulfuric acid is cooled to 0° C. and 190 parts by weight of the partially acetylated pulp entered therein. The acetylation reaction takes 1½ hours, during which time the peak temperature reached is 45° C. Little cooling of the reaction mixture is necessary to maintain the temperature within the desired limits. At the completion of acetylation, water in an amount sufficient to react with any excess acetic anhydride is added to the reaction mixture together with water for ripening, and the cellulose acetate in solution is ripened or hydrolyzed to the desired acetyl value. When the desired acetyl value is reached, excess water is added to the solution to precipitate the cellulose acetate and the latter is separated from solution, washed and dried.

The cellulose acetate obtained in the manner described is of excellent characteristics and may be employed in the preparation of textile materials, film, foils, molding powders, coating compositions and the like.

While our invention has been more particularly described in connection with the preparation of cellulose acetate from partly acetylated purified wood pulp cellulose, wood pulp cellulose partly esterified with other lower aliphatic acids may be employed in like manner for the preparation of other organic esters of cellulose. Thus, in accordance with our invention the wood pulp cellulose may be partly esterified and purified, as described, employing other aliphatic acids such as, for example, propionic acid or butyric acid, or mixtures of each of said acids with acetic acid or with each other. In this manner, other cellulose esters such as, for example, cellulose propionate, cellulose butyrate, cellulose acetate-propionate and cellulose acetate-butyrate may be prepared from wood pulp cellulose partly esterified with said acids or mixtures thereof.

While the partially esterified cellulose of relatively low degree of esterification yields cellulose esters of excellent characteristics on further esterification, as heretofore described, we have found that said partially esterified cellulose is also of unusual value as a paper making material. The partially esterified cellulose may be employed alone or mixed with other fibers such as those of chemical or mechanical wood pulp, or rag fibers such as linen and the like, and the resulting material yields an excellent paper stock. Partially acetylated cellulose of an acetyl value of 5 to 10% possesses unusually desirable properties for use in paper making.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention, what we desire to secure by Letters Patent is:

1. In a process for the preparation of an organic ester of cellulose of relatively high degree of esterification, the steps which comprise digesting comminuted wood with a lower aliphatic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partially esterified, removing the lower aliphatic acid and the material dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acyl groups gained during the digesting step, subjecting said partially esterified cellulose to further esterification.

2. In a process for the preparation of organic esters of cellulose of relatively high degree of esterification, the steps which comprising digesting comminuted wood with a concentrated lower aliphatic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partly esterified, removing the lower aliphatic acid and the material dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acyl groups gained during the digesting step, subjecting said partly esterified cellulose to further esterification.

3. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with acetic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partly acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partly acetylated cellulose to further acetylation.

4. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with concentrated acetic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partly acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partly acetylated cellulose to further acetylation.

5. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with glacial acetic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partially acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partially acetylated cellulose to further acetylation.

6. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with glacial acetic acid at a temperature of from 130 to 220° C. whereby the wood is pulped and the cellulosic constituents thereof partially acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partially acetylated cellulose to further acetylation.

7. In a process for the preparation of cellulose

acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with glacial acetic acid at a temperature of from 130 to 220° C. for from 1 to 10 hours whereby the wood is pulped and the cellulosic constituents thereof partially acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partially acetylated cellulose to further acetylation.

8. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with glacial acetic acid at a temperature of from 130 to 220° C. for from 1 to 10 hours whereby the wood is pulped and the cellulosic constituents thereof partially acetylated to an acetyl value of from 5 to 18% calculated as acetic acid, removing the acetic acid and the materials dissolved therein from the cellulosic constituents and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partially acetylated cellulose to further acetylation.

9. In a process for the preparation of an organic ester of cellulose of relatively high degree of esterification, the steps which comprise digesting comminuted wood with a lower aliphatic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partially esterified, removing the lower aliphatic acid and the material dissolved therein from the cellulosic constituents, chlorinating and bleaching the same and, while said cellulosic constituents still retain substantially all of the acyl groups gained during the digesting step, subjecting said partially esterified cellulose to further esterification.

10. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with acetic acid at a temperature of at least 130° C. whereby the wood is pulped and the cellulosic constituents thereof partly acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents, chlorinating and bleaching the same and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, subjecting said partly acetylated cellulose to further acetylation.

11. In a process for the preparation of cellulose acetate of relatively high degree of acetylation, the steps which comprise digesting comminuted wood with glacial acetic acid at a temperature of from 130° to 220° C. for from 1 to 10 hours whereby the wood is pulped and the cellulosic constituents thereof partially acetylated, removing the acetic acid and the materials dissolved therein from the cellulosic constituents, chlorinating and bleaching the same and, while said cellulosic constituents still retain substantially all of the acetyl groups gained during the digesting step, further acetylating the partially acetylated cellulose.

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