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TREATMENT OF WOOD PULP

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This invention relates to the treatment of wood pulp and relates more particularly to the treatment, by bleaching operations, of unbleached partially esterified wood pulp.

An object of this invention is the preparation of organic esters of cellulose of improved clarity and color from partially esterified wood pulp by steps which include bleaching the same in a novel manner.

Another object of this invention is to provide an improved process for the treatment of partially esterified, unbleached wood pulp whereby the color of the latter may be substantially improved without removing the acyl groups attached thereto.

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

Partially esterified 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 with acetic acid or other lower aliphatic acid at elevated temperature and pressure. The partially esterified wood pulp produced has a substantial number of acyl groups combined therewith. The pulp is washed with lower aliphatic acid until free from soluble reaction products, or with water until neutral. On further esterification the partially esterified wood pulp may be converted into cellulose esters of a higher degree of esterification.

We have now discovered that by treating partially esterified wood pulp, prepared as described, by a novel bleaching process the color thereof may be substantially lightened without effecting any reduction in the acyl groups present. On further esterification, the partially esterified, bleached pulp yields organic esters of cellulose of excellent characteristics. In accordance with our novel bleaching process this desirable effect may be achieved if the partially esterified wood pulp is treated with a solution of peracetic acid, or other lower aliphatic peracid, in acetic acid, or other lower aliphatic acid. This treatment effects a very marked bleaching of the partially esterified pulp. The bleaching action of the peracid may be greatly accelerated, however, if there is added to the treating solution a catalyst comprising a lower aliphatic acid salt of a metal such as, for example, lead, zinc, cobalt, nickel, chromium, manganese and sodium. Examples of suitable salts which may be added to the treating solution are lead acetate, zinc acetate, cobaltous acetate, nickel acetate, chromic acetate, manganous acetate, sodium acetate, sodium propionate, sodium butyrate, lead propionate, lead butyrate, zinc

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propionate, zinc butyrate, cobaltous propionate, cobaltous butyrate, nickel propionate, nickel butyrate, chromic propionate, chromic butyrate, manganous propionate and manganous butyrate. In lieu of adding a metal salt of a lower aliphatic acid to the solution, we may add the metal as a compound which under the conditions employed is converted to a lower aliphatic acid salt. Such compounds are, for example, the metal oxides and carbonates soluble in the solution, as well as metals in such state of combination as, for example, potassium permanganate and potassium dichromate. These compounds are converted under the conditions employed to lower aliphatic acid salts. Employing potassium dichromate chromic acetate is formed, while employing potassium permanganate manganous acetate is formed. Optimum results are achieved, however, employing as catalysts the metals directly in the form of their lower aliphatic acid salts.

The peracid employed for the treatment of the partially esterified pulp may be from 10 to 40% on the weight of the pulp, but optimum results are achieved employing peracetic acid in amounts of from 20 to 40% on the weight of the pulp. Usually, from 10 to 30% of peracetic acid, based on the weight of the pulp, is consumed in the bleaching operation.

The catalyst added to the peracid solution to aid the bleaching process may comprise from 0.5 to 15% on the weight of the pulp calculated as the metal contained in the catalyst. The quantity added varies with the particular catalyst being employed. Thus, for example, employing zinc acetate, an effective quantity of catalyst is that amount containing about 2.5% of zinc on the weight of the dry pulp. Where lead acetate is used, we have found that an amount containing about 9 to 10% of lead on the weight of the pulp yields optimum results, while in the case of manganous acetate a quantity containing about 1.4% of manganese on the pulp is preferable.

The temperature of the peracid solution during the treatment may be from 15 to 115° C. but room temperatures, i. e. about 20 to 25° C. are generally preferred. The bleaching of the partially esterified pulp may be effected in from 5 to 24 hours but in some instances the bleaching may be extended to about 96 hours.

Any suitable lower aliphatic acid may be employed as solvent for the peracetic acid or other lower aliphatic peracid in our novel bleaching process. The acid may be acetic acid, propionic acid, butyric acid and the like. The acids are preferably employed in a relatively concentrated

form, i. e. of a concentration of 50 to 95%. For example, where acetic acid is employed, glacial acetic acid may be used, but the acid is preferably of a concentration of 85 to 95%, the diluent, of course, being water. The proportion of the acetic acid to the pulp being treated is usually of the order of 10 to 100 parts by weight of acetic acid per part by weight of pulp.

In order further to illustrate our invention but without being limited thereto the following examples are given:

Example I

138 parts by weight of dry, partially acetylated wood pulp of an acetyl value of 25.2%, calculated as acetic acid, are entered into a bleaching bath comprising 51.7 parts by weight of peracetic acid, 12,300 parts by weight of 95% acetic acid and 3.6 parts by weight of zinc as zinc acetate. The bath is held to a temperature of about 25° C. and the pulp maintained therein for 68 hours. At the end of this period the pulp is removed, washed and dried. The acetyl value is unchanged but the color is substantially lighter.

The partially acetylated wood pulp employed is produced by digesting wood chips in a sealed digester under autogenous pressure with 85% acetic acid at a temperature of at least 130° C., say 175° C., for about 8 to 15 hours whereby the chips are pulped and the cellulosic constituents are partially acetylated. The partially acetylated pulp produced is then washed neutral employing acetic acid of gradually diminishing strength and may then be bleached as described above in accordance with our novel process.

Example II

146 parts by weight of dry, partially acetylated wood pulp having an acetyl value of 25.2%, calculated as acetic acid, prepared as in Example I, are entered into a bleaching bath comprising 49 parts by weight of peracetic acid, 12,200 parts by weight of 85% acetic acid and 2.0 parts by weight of manganese as manganous acetate. The bath is at room temperature and the partially acetylated pulp is held therein for 24 hours. The color of the pulp is greatly improved by this bleaching operation. The bleached, partially acetylated pulps may then be further acetylated and ripened in the usual manner to yield cellulose acetate of any desired acetyl value.

Example III

137 parts by weight of dry, partially acetylated wood pulp having an acetyl value of 25.2%, calculated as acetic acid, prepared as in Example I, are entered into a bleaching bath comprising 49 parts by weight of peracetic acid, 12,200 parts by weight of 85% acetic acid. No catalyst is added. The pulp is held at room temperature for 96 hours. The pulp is bleached to a considerably lighter color.

While our invention has been more particularly described in connection with the treatment of partially acetylated wood pulp, the process may be advantageously employed in the bleaching of wood pulp partially esterified by means of other organic acids. Examples of such other partly esterified wood pulps which may be bleached in the manner described are those obtained by digesting wood with propionic acid, butyric acid, or mixtures of each of said acids with acetic acid, or with each other. Such digestion processes yield partially esterified cellulose propionate, cellulose butyrate, cellulose aceto-propionate, and cellulose aceto-butyrate, which esters may, as stated, be advantageously bleached to improve their color.

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 improving the color of partially esterified wood pulp obtained by digesting comminuted wood with a lower aliphatic acid, the step which comprises subjecting said partially esterified wood pulp to the action of a bath comprising a lower aliphatic peracid and a lower aliphatic acid in a concenteration of from 50 to 95%, whereby the wood pulp is bleached.

2. In a process for improving the color of partially esterified wood pulp obtained by digesting comminuted wood with a lower aliphatic acid, the step which comprises subjecting said partially esterified wood pulp to the action of a bath comprising peracetic acid and a lower aliphatic acid in a concentration of from 50 to 95%, whereby the wood pulp is bleached.

3. In a process for improving the color of partially esterified wood pulp obtained by digesting comminuted wood with a lower aliphatic acid, the step which comprises subjecting said partially esterified wood pulp to the action of a bath comprising peracetic acid and acetic acid in a concentration of from 85 to 95%, whereby the wood pulp is bleached.

4. In a process for improving the color of partially esterified wood pulp obtained by digesting comminuted wood with a lower aliphatic acid, the step which comprises subjecting said partially esterified wood pulp to the action of a bath comprising a lower aliphatic peracid, a lower aliphatic acid in a concentration of from 50 to 95% and, as catalyst, a metal salt of a lower aliphatic acid.

5. In a process for improving the color of partially esterified wood pulp obtained by digesting comminuted wood with a lower aliphatic acid, the step which comprises subjecting said partially esterified wood pulp to the action of a bath comprising a lower aliphatic peracid, a lower aliphatic acid in a concentration of from 50 to 95% and, as catalyst, a metal compound selected from the group consisting of a metal salt of a lower aliphatic acid and metal compounds convertible to said salts in the bath employed, whereby the wood pulp is bleached.

6. In a process for improving the color of partially esterified wood pulp obtained by digesting comminuted wood with a lower aliphatic acid, the step which comprises subjecting said partially esterified wood pulp to the action of a bath comprising peracetic acid, a lower aliphatic acid in a concentration of from 50 to 95% and, as catalyst, a metal compound selected from the group consisting of a metal salt of a lower aliphatic acid and metal compounds convertible to said salts in the bath employed, whereby the wood pulp is bleached.

7. In a process for improving the color of partially acetylated wood pulp obtained by digesting comminuted wood with acetic acid, the step which comprises subjecting said partially acetylated wood pulp to the action of a bath comprising peracetic acid, acetic acid in a concentration of from 85% to 95% and, as catalyst, the acetic acid salt of a metal, whereby the wood pulp is bleached.

8. In a process for improving the color of partially acetylated wood pulp obtained by digesting

comminuted wood with acetic acid, the step which comprises subjecting said partially acetylated pulp to the action of a bath comprising from 10 to 40% by weight of peracetic acid on the partially acetylated pulp, acetic acid in a concentration of from 85 to 95% and, as catalyst, the acetic acid salt of a metal, whereby the wood pulp is bleached.

9. In a process for improving the color of partially acetylated wood pulp obtained by digesting comminuted wood with acetic acid, the step which comprises subjecting said partially acetylated wood pulp to the action of a bath comprising from 10 to 40% by weight of peracetic acid on the partially acetylated pulp, acetic acid in a concentration of from 85 to 95% and, as catalyst, from 0.5 to 15% on the weight of the pulp of a metal as an acetic acid salt, whereby the wood pulp is bleached.

10. In a process for improving the color of partially acetylated wood pulp obtained by digesting comminuted wood with acetic acid, the step which comprises subjecting said partially acetylated wood pulp to the action of a bath comprising from 10 to 40% by weight of peracetic acid on the partially acetylated pulp, acetic acid in a concentration of from 85 to 95% and, as catalyst, from 2 to 5% on the weight of the pulp of zinc, as zinc acetate, whereby the wood pulp is bleached.

11. In a process for improving the color of partially acetylated wood pulp obtained by digesting comminuted wood with acetic acid, the step which comprises subjecting said partially acetylated wood pulp to the action of a bath comprising from 10 to 40% by weight of peracetic acid on the partially acetylated pulp, acetic acid in a concentration of from 85% to 95% and, as catalyst, from 1 to 3% on the weight of the

pulp of manganese, as manganous acetate, whereby the wood pulp is bleached.

12. In a process for improving the color of partially acetylated wood pulp obtained by digesting comminuted wood with acetic acid, the step which comprises subjecting said partially acetylated wood pulp to the action of a bath comprising from 10 to 40% by weight of peracetic acid on the partially acetylated pulp, acetic acid in a concentration of from 85 to 95%, and, as catalyst, from 2 to 10% on the weight of the pulp of lead, as lead acetate, whereby the wood pulp is bleached.

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