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METHOD OF REFINING KRAFT WOOD PULP
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This invention relates to the preparation from kraft wood pulp of a cellulose product useful as the starting material in an acylation process which comprises treating the pulp with strong aqueous alkali containing a boron compound at moderate temperature and treating the pulp with dilute aqueous alkali at an elevated temperature for the extraction of undesired materials therefrom.

At the present time, probably the most important methods of making chemical wood pulp are the sulfite and the kraft pulping procedures. Up to now, most, if not all, of the wood pulps considered as useful as starting materials for making cellulose esters have been sulfite pulps. Heretofore, refined kraft pulps have not been particularly susceptible to acylation, the cellulose esters prepared therefrom having been characterized by high haze and opaquing properties. Hence, even though kraft cooking procedures are useful in the reclaiming of the cellulose from wood, the cellulose product has been useful only for purposes for which extensive refinement is not required.

One object of our invention is to provide a procedure for the refinement of kraft wood pulp by which that pulp can be readily converted into acetylated cellulose from which dopes of good color and clarity can be obtained. Another object of our invention is a procedure for the refinement of kraft pulp which includes the use of boron compounds therein. Another object of our invention is to provide a combination of steps for refining kraft pulp compatible with other pulp refining steps, whereby products of good properties and good color may be obtained. Other objects of our invention will appear herein.

We have found that kraft pulp forms a product which is susceptible to alkaline refining at moderate temperatures providing the alkali solution employed contains a substantial percentage of boron compound, such as sodium meta-borate, borax or boric acid, which treatment is followed or preceded by an extraction procedure using dilute alkali solution at high temperatures. We have found that by so refining kraft pulp the product obtained will exhibit good activity when subjected to an acetylation procedure and the esterification mass obtained upon using so refined kraft pulp will have good haze and color characteristics indicating substantial esterification and a good cellulose ester product. If the kraft pulp being refined is a bleached pulp the desired product may be obtained merely by a sequence of alkaline refining steps in accordance with our invention. If, however, the kraft pulp to be refined is unbleached it is desirable that the alkaline refining steps in accordance with our invention be interspersed with bleaching steps, such as with aqueous chlorine, sodium hypochlorite, chlorine dioxide or the like. Our invention is adapted for refining kraft pulps prepared not only from spruce but from other woods, such as hemlock, southern pine, alder, maple, gumwood, or other types of wood the fibers of which have been liberated by cooking with a kraft cooking liquor.

In its broadest aspects, our invention involves the subjecting of kraft pulp to a sequence which includes the steps of treating the pulp with a strong alkaline solution containing a low proportion of a boron compound, such as boric acid or $\text{Na}_2\text{B}_4\text{O}_7$ at near normal temperatures and extraction with a hot dilute alkali solution. The treatment may involve a treatment once with this combination or a treatment several times with a refining operation in

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which these steps are used. The treatment may involve treatment with strong alkali and boron compound at moderate temperature followed by treatment with dilute aqueous alkali at elevated temperature and a subsequent treatment with strong alkali and boron compound again at moderate temperature. The alkaline refining steps may be separated by chlorination or bleach treatments. The pulp may be first chlorinated, then treated with a boron containing concentrated alkaline solution, then thickened, then given a high temperature digestion with dilute alkali, again thickened and then treated with a strong boron-compound containing sodium hydroxide solution. The digestion steps can be carried out at atmospheric pressure or above atmospheric pressure. Continuous treatments and re-use of solutions may be resorted to in processing the pulp, particularly if continuous operations are thought to be desirable.

In carrying out our invention the strong alkali treatment is ordinarily carried out with aqueous sodium hydroxide having a concentration within the range of approximately 8–12% which solution contains 2–5% of sodium borate, boric acid or borox (sodium tetraborate). The treatment with the strong alkali is carried out at a temperature within the range of 10–40° C., the pulp being agitated therein for the desired time. For instance, if the strong alkali treatment is to be given once or twice, a time of 1–3 hours may accomplish the desired result. On the other hand, if several treatments are to be given the length of time of each treatment may desirably be modified to the use of shorter periods for each treatment. The pulp after (or before) it has been subjected to the treatment with strong alkali and to the desired chlorinations or bleaching treatments, is treated with dilute aqueous alkali, the sodium hydroxide therein being within the range of ½–2%, the treatment being carried out at a temperature within the range of approximately 100–140° C. Further treatments of the pulp with strong alkali and boron-compound at moderate temperatures, with dilute alkali at elevated temperatures or with combinations of those steps may be given, which steps may or may not be interspersed with treatments with chlorine or with chlorine compounds (such as sodium hypochlorite, chlorine dioxide or sodium chlorite) or with both at an acid pH or at an alkaline pH.

After the pulp has been refined it is washed free of chemicals with water and may be dried or it may be employed directly for acetylation purposes. In the latter case, it would be desirable to remove the water from the cellulose by displacement with acetic acid or some other lower fatty acid giving a pulp wet with fatty acid in good condition for reaction with acetic anhydride or other esterification reagents.

The following examples illustrate a comparison of the procedures in accordance with our invention with those omitting boron compounds and the properties obtained upon acetylating the products refined thereby with those not in accordance with the invention.

Example 1

Unbleached kraft pulp prepared by cooking spruce wood with an alkaline sulfate cooking liquor was subjected to a series of steps in the following sequence:

- (a) 3% aqueous chlorine at 20° C.
- (b) 12% sodium hydroxide solution containing 3% H_3BO_3 for 2 hours at 30° C.
- (c) 3% aqueous chlorine solution at 20° C.
- (d) An aqueous solution of sodium hydroxide of 1% concentration for 2 hours at 100° C.
- (e) An aqueous solution containing 1% sodium chlorite and 5% of acetic acid for 3 hours at 85° C.
- (f) An aqueous solution of sodium hydroxide in 12%

concentration containing 3% of H_3BO_3 for 2 hours at 30° C.

(g) 1% sodium chlorite and 5% acetic acid in water at 85° C. for 3 hours.

(h) Aqueous HCl in 0.5% concentration for 1 hour at 25° C.

The resulting refined pulp was washed and dried and was acetylated in a sigma bladed jacketed mixer as follows:

3 pounds of pulp with a moisture content of 3 to 4% was presoaked for 30 minutes at 105° F. with 6 pounds of glacial acetic acid containing sufficient water to adjust the moisture content of the pulp to 6%. Then 10 pounds of glacial acetic acid and 4 cc. of sulfuric acid were added and the mass was held 15 minutes at 102 to 105° F. The temperature was reduced to 78° F. over a period of 15 minutes and 7.8 pounds of acetic anhydride was added. The mass was cooled to 55° F. and a solution of 90 cc. acetic acid and 41 cc. sulfuric acid was added and the temperature was increased to 102° F. over a period of 75 minutes. The cellulose dissolved in the esterification liquid. The mass was diluted with 10 pounds of aqueous acetic acid to destroy any unused anhydride and the properties of the product were determined. It was found to have a haze of 17 cm. determined by the stainless steel wire test or of 30 p.p.m. when determined against standards made up from water and opaque material. The color was 300.

Example 2

The preceding sequence was repeated using sodium tetraborate instead of boric acid in steps (b) and (f). Testing of the product gave the following values: haze—21 cm. by the stainless steel wire test or 30 p.p.m. when judged against standards made up from water and opaque materials and a color of 300.

Example 3 (Omitting Boron Compounds)

Unbleached spruce kraft pulp was treated by the same sequence as listed in Example 1 but the boron compounds were omitted. The haze was 6 cm. by the stainless steel wire test or 100 p.p.m. by the standards test and the color was 500.

The refined pulp used here exhibited poor activity upon esterification in comparison with the susceptibility to esterification of the pulps obtained by the refinement methods employed in Examples 1 and 2.

A commercial acetylation cellulose made by the alkaline refinement of spruce sulfite pulp was acetylated in a manner similar to that described in the foregoing examples. The properties exhibited by the acetylated pulp were as follows: Haze—10–12 cm. by the stainless steel wire test or 60 p.p.m. by the standards test and a color of 250.

Example 4

Unbleached kraft pulps from other woods than spruce were treated by a procedure embodying the applicants' invention in which the pulp was treated first with chlorine and then repetitively as shown:

(a) 12% NaOH solution containing 3% H_3BO_3 , 30° C., 2 hours.

(b) 1% NaOH, 100° C., 2 hours.

(c) 0.5% sodium chlorite and 5% acetic acid, 85° C., 3 hours.

These pulps were treated by the application of 2 sequences and by the application of 3 sequences respectively and the refined pulps thus obtained were acetylated by a procedure similar to that of the preceding examples.

Number of Treatments.....	2		3	
	Haze, cm.	Color	Haze, cm.	Color
Wood type				
Hemlock.....	19	185	26	115
Southern Pine.....	7	285	15	275
Alder.....	15	235	33	110
Maple.....	12	550	17	245
Gumwood.....	7	375	15	275
Comparison—commercially refined Spruce sulfite pulp acetylated similarly.....			11	170

In the testing of the acetylation products the haze was determined by means of a length of 16 gauge stainless steel wire, the haze number being the length of wire which was inserted into a tube of the cellulose ester dope until the end of the wire became invisible, these tests being run in an apparatus especially constructed for this test. The measurements of haze by the water standards were carried out by comparing the solutions against standard solutions made up from water and precipitated fuller's earth in accordance with the Turbidity Standard for Water Analysis, APHA specifications.

The color determinations were made by comparing cellulose ester solutions with color standard solutions. These are prepared from a color standard containing 500 p.p.m. of platinum purchased as platinum cobalt (APHA Color Standard). The solution may also be prepared as described in "Technical Methods of Analysis" by Roger C. Griffin, page 673 (McGraw-Hill, 1927), which preparation involves dissolving 1.245 grams of potassium platinum chloride containing 0.500 gram of platinum and 1.000 gram of crystallized cobalt chloride ($CoCl_2 \cdot 6H_2O$) containing 0.248 gram of cobalt in water and adding 100 ml. of concentrated HCl and diluting with 1 liter of water. Color standards containing 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 225, 250, 275, 300, 350, 400, 450, 500 and 550 parts per million of platinum were prepared by diluting suitable aliquots of the standard solutions to 500 ml. with water. These standards were placed in bottles of good clarity and free from flaws. The tests were run by passing light from a uniform light source through the sample to be tested and through the color standards more nearly corresponding thereto in color. When a color determination is not clearly like either of two color standards the color number is extrapolated between the two color standards most closely resembling the sample being tested.

Refined pulps in accordance with our invention are useful not only for the preparation of cellulose acetates but for the preparation of other lower fatty acid esters of cellulose, such as cellulose acetate propionate, cellulose acetate butyrate, cellulose butyrate or the like by conventional esterification procedures. The thus prepared cellulose esters are characterized by their usefulness for making up solutions in organic solvents of good clarity and uniformity. These esters are useful for the preparation of sheeting, yarn, molded products and the like, as described in the literature.

The application of various chlorine-containing bleaches to wood pulp is well known in the pulp refining art and where bleaching steps are referred to unless the conditions are given, the conditions used are those conventionally employed in the pulp bleaching operations of the type referred to.

The kraft pulp which is refined in accordance with our invention is to be understood to include any wood pulp prepared from soft wood or hard wood prepared by a sulfate cooking process. This includes not only undercooked stock but as well that which has been given a longer time of cooking.

It is to be understood that in the refining procedure in accordance with our invention it is desirable to follow the customary procedure of subjecting the pulp to a wash-

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ing treatment after each of the steps in the refining operation. It may some time be desirable to carry over the treating material from one step to the other which option, of course, is left to the judgment of the individual operator in performing the refining operations.

We claim:

1. A method of preparing refined kraft wood pulp useful as a starting material in the preparation of cellulose ester products which comprises subjecting kraft pulp to a series of treatments at least two of the steps of which involves (1) treating the pulp with aqueous caustic alkali of ½-2% concentration at 100-140° C., and (2) treating with aqueous caustic alkali of 8-12% concentration containing 2-5% of a boron compound selected from the group consisting of sodium meta-borate, borax and boric acid.

2. A method of refining kraft wood pulp to render it useful as a starting material for cellulose esterification processes which comprises subjecting the pulp in unbleached form to a series of treatments including the steps of (1) bleaching with a chlorine compound, (2) treating with aqueous caustic alkali of 8-12% concentration containing 2-5% of a boron compound selected from the group consisting of sodium meta-borate, borax and boric acid at 10-40° C., and (3) treating with aqueous caustic alkali of ½-2% concentration at 100-140° C.

3. A process of refining kraft pulp to adapt it for use as a starting material for cellulose esterification processes which comprises subjecting unbleached kraft pulp to a series of steps including (1) bleaching with a chlorine compound, (2) treating with aqueous caustic alkali of 8-12% concentration containing 2-5% boric acid at 10-40° C., and (3) treating with aqueous caustic alkali of ½-2% concentration at 100-140° C.

4. A process of refining kraft pulp to adapt it for use as a starting material for cellulose esterification processes which comprises subjecting unbleached kraft pulp to a series of steps including (1) bleaching with a chlorine compound, (2) treating with aqueous caustic alkali of 8-12% concentration containing 2-5% sodium tetraborate

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at 10-40° C., and (3) treating with aqueous caustic alkali of ½-2% concentration at 100-140° C.

5. A method of refining kraft pulp which comprises treatment of the pulp with aqueous caustic alkali of 8-12% concentration containing 2-5% of a boron compound selected from the group consisting of sodium meta-borate, borax and boric acid at 10-40° C. and subsequently treating the pulp with aqueous caustic alkali of ½-2% concentration at 100-140° C.

6. A process of refining kraft pulp to adapt it for use as a starting material for a cellulose esterification process which comprises subjecting the pulp to the following series of steps in the order given:

Treating the pulp with 3% aqueous chlorine at 20° C.
Treating with 12% sodium hydroxide solution containing 3% boric acid for 2 hours.

Treating with 3% aqueous chlorine solution at 20° C.
Treating with an aqueous solution of sodium hydroxide of 1% concentration for 2 hours at 100° C.

Treating with an aqueous solution containing 1% sodium chlorite and 5% acetic acid for 3 hours at 85° C.
Treating with an aqueous solution of sodium hydroxide in 12% concentration containing 3% of boric acid for 2 hours at 30° C.

Treating with 1% sodium chlorite and 5% acetic acid in water at 85° C. for 3 hours and treating with aqueous HCl of 0.5% concentration for 1 hour at 25° C.

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