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**COLD CAUSTIC REFINING OF CELLULOSE**

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2 Claims. (Cl. 162-80)

This invention relates to the cold caustic refining of cellulose, and has for its object the provision of an improved cold caustic refining treatment and an improved cellulose product.

This invention is based on my discovery that within certain limits, the mercerizing effect of concentrated cold caustic solutions on native cellulose such as in wood pulp can be inhibited without adverse effect on their solvent power for hemicellulose and other impurities by including a soluble borate in said caustic solutions. Surprisingly, cellulose refined according to the invention retains its native structure known as Cellulose I even when refined with relatively strong cold caustic solutions that normally convert said Cellulose I into Cellulose II or mercerized cellulose. The differences in the physical and chemical properties of native cellulose (Cellulose I) and mercerized cellulose (Cellulose II) and their general fields of utility are well known and described in the literature.

Among the methods available for determining the presence and relative amount of mercerized cellulose (Cellulose II), if any, in a given sample of refined cellulosic material the following three are most commonly used:

(1) *Acetylation of a dried sample of the material.* Mercerization inactivates cellulose towards acetylation; when the mercerized cellulose has been dried, and particularly when it has been dried at an elevated temperature, it is extremely difficult to acetylate by any of the usual methods.

(2) *The O'Connor "Crystallinity" Index.* The O'Connor "Crystallinity" Index is described by O'Connor, R. T., et al., Anal. Chem. 29, 998 (1957). In using this method, infrared absorption spectra are prepared by the O'Connor process. The ratio between the absorbences of the peaks at about 1430  $\text{cm}^{-1}$  and 890  $\text{cm}^{-1}$  provides an excellent measure of the degree of mercerization of the cellulose.

(3) *Determination of limit I.V.'s.* Mercerization changes the basic structure of a native cellulose (Cellulose I) to that of mercerized cellulose (Cellulose II). The results is a sharp drop in the limit I.V., usually without any corresponding drop in the ordinary I.V. A sharp drop in limit I.V.'s (with or without a corresponding drop in regular I.V.) accordingly affords a sensitive and accurate method of detecting and measuring mercerization in a sample of cellulose.

In the cold caustic refining of wood pulp and other types of cellulosic material, mercerization normally starts at a caustic concentration of about 6 to 7 percent at room temperature and will be substantially complete at about 9 to 12 percent. These percentages can be raised and lowered somewhat by variations in origin and pretreatment of the cellulose and by variations in temperature. Normally, mercerization increases with rising concentration and decreases with rising temperature and vice versa. On the whole, however, the foregoing range holds very well for normal cold caustic refining sequences as presently used.

Cold caustic refining sequences using mercerizing concentrations of caustic (7 to 8 percent and up) have many advantages when compared with corresponding but more drastic high temperature sequences. Other things being equal, they provide a better yield of a less degraded and more highly refined, higher alpha cellulose product. Refined celluloses of this type accordingly are widely

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used for xanthation, etherification, etc., where mercerization is not detrimental to processing. In refining cellulosic materials with cold caustic solutions, the efficiency of the refining action depends to a large extent upon the concentration of the cold caustic in said solution. Experience has shown that the most effective action is attained with from about 8 to 14 percent caustic present on the weight of the solution.

In spite of the very real advantages provided by using mercerizing concentrations of caustic in cold caustic refining of cellulose, it has not been possible to use them when preparing dried cellulosic products for acylation purposes. Mercerized fiber seems to close up and become hornified to a certain extent upon drying which renders it inactive towards the relatively large "acyl" groups. While solvent displacement methods of acylating "never dried" mercerized cellulosic fibers are known, they have never found favor in commerce. For reasons of economy, convenience in handling and stability in storage wood pulps whether in sheet or crumb form are always dried (usually over the hot rolls of a pulp drying machine) before use. This fact has ruled out the use of mercerized fiber in the acylation marked in the past.

A great deal of time, effort and money have been spent in vain over the years seeking some practical method of overcoming the inactivating effect drying has on mercerized pulp for acylation purposes. It has always been found necessary to avoid any trace of mercerizing. This has been done by holding the caustic level in any cold caustic solutions applied to the fiber below 6 to 7 percent. Caustic over that level, no matter for how brief a time it contacts the fiber, has a detrimental effect on the reactivity of the final product towards acylation when dried. This is true in spite of the superior refining action of the more concentrated cold caustic and the more refined product with its higher alpha content. Applicant's discovery provides the first practical break-through in this barrier. Using it, one simply incorporates borate ions, either as soluble borate or as boric acid, in the cold caustic solution and then the total caustic concentration can be raised as high as 10 to 16 percent total titratable alkali without its having any mercerizing effect on the fiber and without any impairment of the increased refining power of the more concentrated caustic solution. The process of this invention thus achieves the unexpected result of yielding a high alpha, cold-caustic refined wood pulp or other cellulosic material that can be dried and still be amendable to efficient acylation. For example, it provides a purer, more highly refined dry wood pulp that acetylates to form an improved cellulose acetate with a better haze, color and clarity than it has been possible to obtain with any other dry acetylation pulp heretofore produced. Significantly, also, the degree of refining accomplished by the more concentrated cold caustic solution is not decreased by the presence of the borate ions.

The amount of boric acid or solution borate required to inhibit the mercerizing action of a given cold caustic solution on a given native cellulose varies with the concentration of the caustic in the refining solution. For caustic solutions containing 10 percent total titratable alkali expressed as percent NaOH, it will be found that from 6.0 to 8.0 percent borax, or equivalent boric acid, is required to prevent mercerization and still obtain good purification. With increasing concentrations of caustic, more borax, or boric acid, will be required until for solutions containing 16 percent total titratable alkali, as much as 25.5 to 27.5 percent borax, or equivalent boric acid, should be present. Other than the presence of the borate ion in the solution, no change in the normal processing sequence is needed. Total titratable alkali is defined as the amount of alkali, expressed as NaOH,

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that can be measured by titrating to pH 7 with a standard acid solution.

The process of the invention is carried out in the temperature range of from 5° to 50° C., in a caustic solution containing from 10 to 16 percent total titratable alkali with from 6 to 28% by weight of a boron compound of the group consisting of sodium meta-borate, borax and boric acid, in which the boron compound is expressed as sodium tetra-borate (borax).

The preferred and advantageous caustic refining solutions for a refining process of the invention, at a temperature of 35° C., are shown in the following table:

Total Titratable Alkali Expressed As Percent NaOH	Boron Compound Expressed As Percent Borax Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O
10	6.0 to 8.0
11	9.2 to 11.2
12	12.4 to 14.6
13	15.7 to 17.8
14	19.0 to 21.0
15	22.2 to 24.2
16	25.5 to 27.5

When the process is carried out at lower temperatures, the amount of boron compound should be increased, and may be decreased for higher temperatures.

The following examples illustrate operations carried out in accordance with the invention and characteristics of the resulting products.

#### EXAMPLE I

A large sample of partially bleached southern pine, dissolving-grade sulfite wood pulp was obtained from the middle stage refining section of a pulp mill. At the time this sample was taken it had received the following treatment:

Digestion of the pulp to a Tappi I.V. of 8.44 and a Tappi K number of 8.6, washing, a chlorination treatment and another washing, and a hot dilute caustic (NaOH) extraction and washing.

Without drying, the partially bleached wood pulp was divided into seven portions which were treated as follows:

*Portion A.*—This portion of the pulp sample was used as a control. It was given a standard ClO<sub>2</sub> bleach and washed. It was then made into handsheets on a suction mold and dried in an oven at 60° C. for testing.

*Portion B.*—This portion of the pulp sample was extracted at a consistency of 3 percent for 4 minutes at a temperature of 35° C., with a caustic solution containing 8 percent NaOH on the weight of said solution. The extracted pulp was then washed and given the same ClO<sub>2</sub> bleach, etc., as Portion A.

*Portion C.*—This portion of the pulp sample was treated exactly the same as Portion B, except that the 8 percent alkaline extraction solution also contained 2.9 percent borax on the weight of the solution.

*Portion D.*—This portion of the pulp sample was treated exactly the same as Portion B, except that the 8 percent alkaline extraction solution was increased to 9 percent total titratable alkali on the weight of said solution.

*Portion E.*—This portion of the pulp sample was treated exactly the same as Portion C, except that the concentration of the alkaline extraction solution was raised to 9 percent total titratable alkali and 3.9 percent borax on the weight of said solution.

*Portion F.*—This portion of the pulp sample was treated exactly the same as Portion B, except that the alkaline concentration in the extraction solution was increased to 10 percent total titratable alkali on the weight of said solution.

*Portion G.*—This portion of the pulp sample was treated exactly the same as Portion C, except that the concentration of the extraction solution was 10 percent

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total titratable alkali and 6.7 percent borax on the weight of said solution.

The following table gives the results of various standard tests as made on the foregoing pulp samples after they had been treated as indicated.

Sample	Percent NaOH						
	None	8		9		10	
	A <sup>1</sup>	B	C	D	E	F	G
I.V. (Regular)	6.76	6.32	7.36	5.62	7.58	5.30	6.12
I.V. (Limit)	1.33	1.13	1.18	0.94	1.16	0.78	1.14
Alpha, percent	92.3	95.7	95.3	96.6	95.9	98.0	96.9
Xylan, percent	1.8	0.5	0.8	0.4	0.6	0.4	0.6
Mannan, percent	2.2	1.2	1.4	1.1	0.9	0.9	0.8
G.E. Brightness	94.5	94.7	94.9	93.8	94.1	93.2	94.7
Crystallinity Index	2.28	2.58	2.32	1.63	2.50	1.42	2.25

<sup>1</sup> Control.

#### EXAMPLE II

A large sample of "never dried," fully bleached, special acetate grade, hemlock, sulfite pulp was obtained and divided into six portions. Each portion was then extracted with one of the caustic solutions as set out in the following table. The consistency of the extractions was 3 percent and the temperature was 35° C. After extraction, each portion was washed with water until neutral and tested for its "crystallinity index" and "limit I.V." by the same methods as used in Example I. The results are tabulated in the following table:

Sample	Extracting Solution		Crystallinity Index	Limit I.V.
	NaOH, Percent	Borax, Percent		
A	8.0	None	2.05	0.95
B	8.0	5.3	2.66	0.98
C	10.0	None	1.59	0.68
D	10.0	6.7	2.50	0.92
E	12.0	None	0.62	0.55
F	12.0	12.5	1.89	0.90

From the foregoing results it is apparent that little or no mercerization has occurred in the portions of pulp which were extracted with the caustic-borate mixtures while a very substantial amount of mercerization was found in those samples where no borate was present. Refining also has not been adversely affected by the presence of the borate to any appreciable extent as shown by the xylan, mannan and G.E. brightness values.

In determining a limit I.V., 0.3 gram of the pulp to be tested is osterized (ground to a fine particle size) and then hydrolyzed for 35 minutes in 75 mls. of 2.0 N HCl at 100° C. The sample is then filtered, washed with water and methanol and dried at 115° C. The normal cuene I.V. test is then run on 0.2 gram of this material.

In determining crystallinity indexes KBr discs are prepared by mixing 1.5 mg. of sample with 300 mg. of KBr in the form of prepressed discs prepared from Harshaw I.R. grade powdered KBr. The use of prepressed KBr discs gave results similar in quality to discs obtainable from 60-80 mesh KBr. The mixture was ground 5 minutes in a "Wig L Bug," placed in the die, evacuated 5 minutes, and pressed 5 minutes at 25,000 pounds gauge pressure. Each disc was next tempered for 15 minutes at 105° C. This caused it to become opaque. After gentle grinding in an agate mortar it was repressed, yielding a stable, transparent disc.

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The crystallinity index was calculated from the absorbance of the bands at 1430 and 890  $\text{cm}^{-1}$ , determined by the baseline technique. Baselines for these two bands were drawn between points at about 1400 and 1500 $^{-1}$ , and at about 850 and 925  $\text{cm}^{-1}$ , respectively.

## EXAMPLE III

The effectiveness of boric acid or borate in preventing mercerization of cellulosic material and the inactivation of said material towards acylation upon its drying is illustrated by this example.

As a base material a sample of unbleached commercial grade southern pine sulfite dissolving pulp was procured from a washer in a pulp mill and without drying was subjected to a mild chlorination, washing and a brief pressure cook at 120° C. with dilute NaOH solution. It was then thoroughly washed and divided into four portions for bleaching as follows:

Portion A was extracted at 30° C. for 3 minutes with a 9% NaOH solution and a consistency of 2%. It was then bleached by one stage of hypochlorite and one stage of chlorine dioxide in the usual manner with thorough washing between and after each stage.

Portion B was extracted at 30° C. for 3 minutes with a 10% NaOH solution and a consistency of 2%. It was then bleached with hypochlorite and chlorine dioxide in exactly the same manner as Portion A.

Portion C was extracted at 35° C. for 3 minutes with a solution containing 10% total titratable alkali and 6.7% borax. It was then bleached with a stage of chlorine dioxide as in Portions A and B above.

Portion D was treated exactly the same as Portion C.

After the foregoing, bleached Portions A, B, C and D were formed into handsheets and air dried to prepare them for acylation by a standardized method used to determine the percent of inactive fiber present in an acylation pulp. In this method carefully prepared samples of the fiber to be tested are acylated in a specified  $\text{H}_2\text{SO}_4$  catalyzed process without pretreatment for 6 hours at 20° C. and then hydrolyzed to the diacetate after the addition of an acetic acid stop acid at 30° C. over a period of 88 hours. The product is then diluted to a low consistency with acetone and the unreacted fibers filtered out and weighed after careful drying. The following table compares the percentage of unreacted fibers in each of the foregoing samples.

	Portion			
	A	B	C	D
Percent Unreacted fiber.....	3.1	56.2	0.07	0.05

## EXAMPLE IV

This example illustrates the improvement in haze and color that is obtained by use of a cellulosic fiber that has been treated according to the process of this invention.

A sample of bleached southern pine acylation grade sulfite pulp was taken from the last bleach washer of a pulp mill. Without drying it was divided into three portions, each of which was treated as follows:

Portion A was formed into handsheets for acylation and dried at 60° C. to approximately 94.0% oven dry as a control sample.

Portion B was extracted with a solution containing 10% total titratable alkali and 6.7% borax at 35° C. for 20 minutes at 3% consistency. It was then thoroughly washed with water, formed into handsheets for acylation and dried at 60° C. to approximately 94.0% bone dry as before.

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Portion C was extracted with a solution containing 10% total titratable alkali, 6.7% borax and 0.5% active chlorine at 35° C. for 20 minutes at 3% consistency. It was then formed into handsheets for acylation and dried at 60° C. to approximately 94.0% bone dry in the same manner as the two previous portions.

Each of the foregoing portions was acetylated and the haze and color determined according to the method set out at ASTM Standard D871. The results are shown in the following table.

	Portion		
	A	B	C
Haze.....	55	15	15
Color.....	370	190	170

## Example V

A supply of unbleached commercial grade southern pine sulfite dissolving pulp was procured from the washer in a pulp mill and without drying subjected to a mild chlorination, washing and a brief pressure cook at 120° C. with dilute NaOH solution. It was then thoroughly washed and divided into four portions for bleaching as follows:

Portion A was extracted at 30° C. and 2% consistency with a 6% NaOH solution for 3 minutes. It was then washed, bleached with hypochlorite, washed, bleached with chlorine dioxide and washed once more. It was then formed into handsheets and dried at 60° C. to about 94.0% oven dry.

Portion B was extracted at 30° C. and 2% consistency with a 10% NaOH solution for 3 minutes. It was then washed, bleached, formed into handsheets for acylation and dried exactly as in Portion A.

Portion C was extracted at 30° C. and 2% consistency with a solution containing 10% total titratable alkali and 6.7% borax for 5 minutes. It was then bleached, washed, formed into handsheets for acylation and dried exactly as in Portions A and B.

Portion D was extracted at 30° C. with a 12% total titratable alkali solution containing 12.4% borax and 0.5% active chlorine (based on pulp) for 60 minutes at a consistency of 12%. It was then washed and bleached with chlorine dioxide, washed, formed into handsheets, and dried for acylation at 60° C. as in the previous cases.

Each portion of bleached pulp was then acetylated by a standard method adapted from an article by C. V. Malm, Ind. and Eng. Chem. 38, 77 (1946). The results are compared in the following table:

	Portion			
	A	B	C	D
Triacetate:				
Haze.....	0.317	0.135	0.073	0.071
Color.....	0.007	0.024	0.037	0.020
Diacetate:				
Acetone Haze.....	0.183	0.136	0.126	0.108
Acetone Color.....	0.051	0.048	0.045	0.037
DMF Haze.....	0.068	0.066	0.053	0.029
DMF Color.....	0.056	0.044	0.025	0.037
Disc Color.....	0.307	0.272	0.237	0.227
False Body Effect, percent.....	85	62	54	66
Plugging Value, gms.....	98	146	227	234

I claim:

1. The process of producing non-mercerized, cold caustic refined, high alpha cellulose from sulfite wood pulp which comprises subjecting said cellulosic material to a refining treatment in an aqueous caustic solution at

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a temperature of from 5° to 50° C. containing from 10 to 16% by weight of total titratable alkali and from 6 to 28% by weight of a soluble borate compound of the group consisting of sodium meta-borate, borax and boric acid, said amount of borate being expressed as percent borax to total titratable alkali according to the following table:

Total Titratable Alkali Expressed As Percent NaOH	Boron Compound Expressed As Percent Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
10	6.0 to 8.0
11	9.2 to 11.2
12	12.4 to 14.6
13	15.7 to 17.8
14	19.0 to 21.0
15	22.2 to 24.2
16	25.5 to 27.5

2. The cold caustic purification of sulfite cellulose wood pulp to produce non-mercerized cellulose which comprises subjecting the wood pulp to a purification treatment at a temperature of from about 30° to 35° C. in a boron containing caustic solution in which the ratio of boron com-

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pond, expressed as percent borax, to total titratable alkali conforms to the following table:

Total Titratable Alkali Expressed As Percent NaOH	Boron Compound Expressed As Percent Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
10	6.0 to 8.0
11	9.2 to 11.2
12	12.4 to 14.6
13	15.7 to 17.8
14	19.0 to 21.0
15	22.2 to 24.2
16	25.5 to 27.5

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