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BLEACHING AND REFINING PROCESS FOR PRODUCING DISSOLVING PULPS

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ABSTRACT OF THE DISCLOSURE

Dissolving pulps suitable for use in the manufacture of viscose rayon are prepared from unbleached sulfite pulps by a bleaching and refining process including the steps of (1) chlorination; (2) combined alkaline hypochlorite dilute caustic extraction; (3) cold caustic extraction with concentrated caustic solution and (4) alkaline hypochlorite treatment.

This invention relates to a process for producing dissolving pulps suitable for use in the manufacture of viscose rayon. More particularly, it relates to a new and improved refining and bleaching process for converting sulfite pulps into viscose grade dissolving pulps.

In producing dissolving pulps for use in the manufacture of viscose rayon, it has been standard practice heretofore to subject highly delignified, soft unbleached pulps from an "acid-sulfite" cooking process to multi-stage bleaching and refining sequences. These bleaching and refining sequences have normally included one or more high pressure, hot caustic extraction stages and excellent dissolved pulps are thereby produced. However, it has been a long standing problem with regard to these conventional techniques that the overall yield of dissolving pulps is low and the equipment and processing costs are relatively high. Additionally, the high toxicity and BOD content of the hot caustic extraction effluents resulting from the hot caustic extraction stages of the heretofore conventional bleaching and refining sequences employed for converting the unbleached pulps to dissolving pulps have required costly chemical recovery and waste liquor disposal systems for environmental protection. As a result of these factors, conventional dissolving pulps for use in the manufacture of viscose rayon have been relatively expensive.

It would therefore be highly desirable and economically important to provide a new and improved process for preparing bleached and refined viscose grade dissolving pulps having relatively low capital requirements and processing costs with an accompanying increase in overall yield of dissolving pulp product. This is particularly true in view of the rapid rise in demand for relatively high quality, substantially lower priced dissolving pulps for conversion into staple fiber for the nonwoven and disposables market.

To this end, considerable research effort has been expended in developing a process for preparing bleached and refined pulps having the requisite processing properties and, at the same time, being relatively low price so that yarns prepared therefrom can compete in the nonwoven and disposables field.

It is therefore an object of the present invention to provide a process for producing high yield, relatively low cost bleached and refined dissolving grade pulps. A related object is to provide a process for producing bleached and refined dissolving pulps suitable from a physical and chemical standpoint as well as a commercial standpoint for use in preparing nonwovens and disposables.

Another object is to provide a process for producing relatively low cost, viscose grade, dissolving pulps without

forming highly toxic, hot caustic extraction effluents as a by-product during the bleaching and refining of the pulps.

A further object is to provide a multi-stage bleaching and refining process for converting unbleached sulfite pulps into viscose grade dissolving pulps.

A still further object is to provide a process for producing relatively high quality bleached and refined dissolving pulps which require a relatively low capital expenditure for processing and environmental protection plants.

Additional objects, if not specifically set forth herein, will be apparent to one skilled in the art from the following detailed description of the invention.

Generally, the process of our invention comprises a new and improved four stage bleaching and refining sequence for converting unbleached sulfite pulps into bleached and refined viscose grade dissolving pulps having the desired physical and chemical characteristics. The pulps produced by our process are particularly well suited for use in preparing viscose filaments and staple fibers for the manufacture of nonwoven and disposable fabrics. Additionally, the bleached sulfite viscose pulps produced by our process are obtained in substantially increased yields as compared with prior art processes. Furthermore, our process does not require a hot caustic extraction stage during refining. Thus, the need for costly, high volume, high pressure, refining equipment which has been required heretofore is eliminated and the production of highly toxic, hot caustic extraction effluents with the attendant disposal problems also is eliminated.

More particularly, our process comprises subjecting a suitable unbleached sulfite pulp to a bleaching and refining sequence including the steps of (1) chlorination; (2) combined alkaline hypochlorite-high consistency, dilute caustic extraction; (3) low consistency extraction with concentrated caustic solution; and (4) alkaline hypochlorite treat.

We have found that particularly desirable sulfite pulps for use in our process are the relatively inexpensive, high yield, easy bleaching, paper grade sulfite wood pulps. Particularly preferred are the unbleached paper grade sulfite pulps prepared by a relatively mild digestion of sulfite-digestible wood chips with a soluble base acid sulfite or bisulfite cooking liquor. In the preparation of these wood pulps the soluble base cooking liquor used for the so-called "acid sulfite" process has a total SO_2 content of about 6.0 to 8.5 percent and a relatively high combined SO_2 content of 0.8 to 1.2 percent, based on the weight of the liquor. Pulping is normally continued for about 5 to 7 hours at about 130° to 150° C. and at a pH of 1 to 2. The digested pulp is then blown out of the digester, washed and dewatered by conventional techniques. Another preferred raw material for use in our process is paper grade sulfite wood pulp prepared by the so-called "bisulfite" process in which the cooking liquor normally has a total SO_2 content of about 3.5 to 5.0 percent and a relatively high combined SO_2 content of about 1.75 to 2.5 percent. Pulping is continued for about 5 to 7 hours at a pH of about 3 to 6 and a temperature of about 150° to 165° C. The pulp is then blown from the digester, washed and dewatered by conventional methods. Both of the foregoing techniques for producing preferred starting materials for our process provide minimum degradation and loss of cellulose and a maximum yield of easy-bleaching paper grade pulp.

In accordance with a preferred embodiment of our invention, an unbleached sulfite pulp is initially treated in a chlorination stage at a consistency of about 3 percent on an oven dried pulp basis, with about 1–5 percent chlorine. This chlorination stage is performed at a pH not greater than about 4.0, preferably in a range of about pH 1.5 to 3.5, at a temperature of about 5–30° C., preferably about

20–30° C. for a period of time sufficient to allow substantial completion of the reaction. This time period will vary depending on factors such as the particular pulp being treated and the processing conditions employed, but normally will not exceed about 60 minutes, preferably about 10–30 minutes.

Following the chlorination stage, the pulp is washed with water and the aqueous pulp suspension then is subjected to a combination hypochlorite-mild caustic extraction stage wherein an alkaline hypochlorite treat is followed immediately without an intervening wash by a high consistency, mild caustic extraction. In the hypochlorite phase of this treatment, an alkaline hypochlorite, for instance an alkali metal or alkaline earth metal hypochlorite, for example sodium or calcium hypochlorite, is added to the washed pulp suspension at a pulp consistency of about 9–17% on an oven dried pulp basis preferably about 12%. An amount of hypochlorite is employed sufficient to provide about 2–3 percent available chlorine based on the weight of the pulp with excess caustic soda being incorporated to maintain the pH at about 10–11 when the hypochlorite is consumed. This treatment is continued until all the hypochlorite is consumed, preferably for a period of about 1–2 hours, at a temperature in the range of about 30–70° C., and preferably about 35° C. At the conclusion of the hypochlorite treat and without an intervening wash, the pulp stock is subjected to a mild caustic extraction with sufficient sodium hydroxide to insure an excess of caustic at the end of treat. Preferably, this mild caustic extraction is carried out at atmospheric pressure with the addition of less than about 4 percent sodium hydroxide (based on the weight of the pulp) and at a temperature of less than about 70° C. for a period of about 1–4 hours depending upon the conditions used. The final pH of this mild caustic treat is again maintained at about 10–11.

The suspension obtained in the combination hypochlorite-mild caustic extraction stage is then washed with water and dewatered. The pulp is then subjected to a cold caustic extraction stage with aqueous caustic soda solution at low pulp consistency to remove hemicelluloses and other carbohydrate impurities. The cold alkali extraction is conducted at a temperature in the range of about 15–50° C., preferably about 15–25° C., under atmospheric pressure with caustic concentration being about 4–11% (on a solution basis) and preferably about 7%, and a consistency of about 3% (based on the weight of the pulp), for about 3–20 minutes.

After washing and dewatering the cold caustic extracted stock, an alkaline hypochlorite solution such as a sodium or calcium hypochlorite solution, having about 2% available chlorine (based on the weight of the pulp) is added to the pulp and a sufficient amount of sodium hydroxide is also added to maintain at all times a pH of at least 7, and preferably about 11. A pulp consistency of about 9–17%, preferably about 12–15%, is also maintained. The temperature is kept between about 30° and 70° C., and preferably about 55° C., and the treatment is continued until the stock has the desired Cuene intrinsic viscosity (about 3–6 I.V.) and brightness (about 90–94 ELB). Normally, this takes about 45–120 minutes depending upon factors such as the pulp employed, the processing conditions used, and the like. The resulting bleached and refined pulp is then dewatered, washed, treated with SO_2 and dried by conventional methods.

The dissolving pulps produced by the process of the present invention have been found to be reactive and xanthate readily into easy filtering viscose solutions suitable for spinning into rayon filament that is particularly useful in preparing nonwoven and disposable fabrics. Additionally, the bleached and refined viscose grade dissolving pulps produced by our process are recovered in substantially higher yields and at lower cost than similar grade pulps produced by prior techniques.

The following examples are set forth for the purpose of illustrating the process of this invention and the characteristics of the resulting products only and are not intended to be construed as being limitative in any respect.

EXAMPLE I

This example is set forth to demonstrate the advantages obtained when the process of the present invention is applied to an unbleached paper grade sulfite wood pulp as compared with a conventional prior art viscose-type bleaching and refining process applied to the same unbleached paper grade pulp.

A batch of Western hemlock wood chips was prepared and cooked to a fairly raw sulfite paper grade pulp by conventional methods using a sodium base acid sulfite cooking liquor. The unbleached pulp which had a Cuene intrinsic viscosity (I.V.) of 11.1 and a permanganate No. (K No.) of 20 was obtained in a screened yield of 46.5 percent (on an oven dried pulp basis). Two samples of this pulp (3 kg. each) were bleached and refined by the following methods:

Method (1).—Normal bleaching and refining process previously employed in the production of viscose grade dissolving pulps

First Stage.—The unbleached pulp was chlorinated by conventional means for 20 minutes at 20° C. with 4 percent added chlorine. The pulp consistency was 3 percent on an O.D. pulp basis. The pulp was then washed, dewatered and passed on to the next stage.

Second stage.—The pulp from the preceding stage was extracted with a 7 percent sodium hydroxide solution at a pulp consistency of 17 percent (O.D. pulp basis) for 45 minutes at 110° C. It was then washed, dewatered and passed on to the next stage.

Third stage.—The pulp from the preceding stage was treated with an alkaline sodium hypochlorite solution containing 2.2 percent of available chlorine and 1.0 percent sodium hydroxide on an O.D. pulp basis. The treatment was for 95 minutes at 60° C. and at a pulp consistency of 15 percent. The bleached pulp was then washed, dewatered, treated with SO_2 to a pH of 2.8 and dried by conventional methods.

Samples of the resulting dissolving pulp were then xanthated by conventional methods into an 8.5/5.25/32 (cellulose/NaOH/CS_2) viscose spinning solution to determine its viscose spinning characteristics. The results obtained are summarized in Table I.

Method (2).—Method of the present invention for bleaching and refining pulps to produce viscous grade dissolving pulps

First stage.—The unbleached pulp was chlorinated in exactly the same manner as in the corresponding section of Method (1) above. The chlorination was continued for 20 minutes at 20° C. using 4 percent added chlorine and a pulp consistency of 3 percent on an O.D. pulp basis. The pulp was then washed, dewatered and passed on to the next stage.

Second stage.—The pulp from the preceding stage was treated with an alkaline sodium hypochlorite solution containing 2.2 percent available chlorine and 1.6 percent sodium hydroxide on an O.D. pulp basis. The consistency was 14 percent and the treatment was continued for 105 minutes at 35° C. Without washing and in the same vessel, 1–3 percent NaOH was then added to the charge, the temperature was raised to 40° C. and the treatment continued for another 105 minutes. The pulp was then washed, dewatered and passed on to the next stage.

Third stage.—The pulp from the preceding stage was extracted for 15 minutes at 25° C. and a pulp consistency of 3 percent (O.D. pulp basis) with a 7.5 percent sodium hydroxide solution. It was then washed, dewatered and washed, dewatered and passed on to the next stage.

Fourth stage.—The pulp from the preceding stage was treated with an alkaline sodium hypochlorite solution containing 2.2 percent available chlorine and 0.9 percent sodium hydroxide on an O.D. pulp basis. The treatment was continued for 70 minutes at 55° C. and the consistency on an O.D. pulp basis was 15 percent. The bleached pulp was then washed, dewatered, treated with SO_2 to a pH of 2.8 and dried by conventional methods.

Samples of the resulting dissolving pulp were then xanthated by conventional methods into an 8.5/5.25/32 viscose spinning solution to determine its viscose spinning characteristics. The results obtained are summarized in Table 1 wherein chemical additions are based on O.D. pulp except where noted.

TABLE 1

Bleaching and refining sequence used	Method (1) normal viscose (control)	Method (2)
Chlorination stage:		
Cl_2 added, percent	4.0	4.0
Time, H:M	0:20	0:20
Temp. ° C	20	20
Consistency, percent O.D	3	3
Alkaline hypochlorite (sodium base):		
Cl_2 added, percent		2.2
NaOH added, percent		1.6
Time, H:M		1:45
Temp., ° C		35
Consistency, percent O.D		[a] 14
Caustic extraction:		
NaOH added, percent	7.0	1.3
Time, H:M	0:45	1:45
Temp. ° C	110	40
Consistency, percent O.D	17	13.3
Cold caustic extraction:		
NaOH added, percent (solution basis)		7.5
Time, H:M		0:15
Temp. ° C		25
Consistency, percent O.D		3
Alkaline hypochlorite (Na-base):		
Cl_2 added, percent	2.2	2.0
NaOH added, percent	1.0	0.9
Time, H:M	1:35	1:10
Temp., ° C	60	55
Consistency, percent O.D	15	15
SO_2 treat:		
Initial pH	2.8	2.8
Overall bleached yield	37.0	38.9
Cuene I.V	4.4	4.4
Brightness, ELB	90.3	91.1
Viscosise, 8.5/5.25/32:		
Viscosity, b.f.s	47.2	81.2
Plugging value, g./cm.^{2} [a]	1,500	2,200

[a] No wash. [b] Values were corrected for viscosity.

As will be noted from the above tabulated results, a substantial increase in yield is achieved employing the process of the present invention as compared with the conventional prior art bleaching and refining process. In fact, employing portions of the same easy bleaching paper grade sulfite pulp, the process of our invention provides a 1.9 percent increase in yield of bleached pulp (based on the weight of the wood used) over the prior art process which amounts to a 5% increase in relative overall yields. Pulp produced by our process also has somewhat better color and higher (improved) plugging value (2200 vs. 1500). Furthermore, since there is no hot caustic, high pressure extraction stage in the process of the present invention there is no toxic, high BOD hot caustic effluent the disposal of which presents an inherent problem with the standard prior art process.

EXAMPLE II

This example is set forth to demonstrate the very substantial increase in bleached yield obtained by applying the process of the present invention to a paper grade sulfite pulp as compared with a conventional prior art process applied to a conventional dissolving grade unbleached pulp.

A batch of wood chips was prepared from Eucalyptus wood and divided into several portions. One portion was cooked to a rather raw paper grade pulp having a K No. of 18.8 and a Cuene I.V. of 12.4. The screened pulp yield was 53.9 percent. Another portion of the chips was cooked to a rather soft rayon grade pulp having a K No. 8.7 and a Cuene I.V. of 8.42 with a screened pulp yield of 48.4 percent. Both batches were cooked by the acid sulfite process using a soda base acid sulfite cooking liquor. The washed unbleached pulps were then bleached and refined by the processes of Example I under the conditions and with the results set forth in Table 2 wherein chemical additions are based on O.D. pulp except where noted.

TABLE 2

Pulp used, bleaching and refining sequence	Dissolving grade (K No. 8.7–I.V. (8.42) Method (1)	Paper grade (K No 18.8–I.V. 12.4) Method (2)
Chlorination stage		
Cl_2 added, percent	2.5	4.6
Time, H:M	0:20	0:20
Temp. ° C	25	25
Consistency, percent O.D	3	3
Alkaline hypochlorite (Na-base):		
Cl_2 added, percent		2.0
NaOH added, percent		1.1
Time, H:M		1:45
Temp. ° C		35
Consistency, percent O.D		[a] 12
Caustic extraction:		
NaOH added, percent	7.5	1.3
Time, H:M	0:45	1:45
Temp. ° C	110	40
Consistency, percent O.D	15	11.8
Cold caustic extraction:		
NaOH added, percent (solution basis)		7.5
Time, H:M		0:15
Temp. ° C		25
Consistency, percent O.D		3
Alkaline hypochlorite (Na-base):		
Cl_2 added, percent	1.7	1.5
NaOH added, percent	1.0	0.9
Time, H:M	1:00	2:00
Temp. ° C	57	55
Consistency, percent O.D	16	15
SO_2 treat:		
Initial pH	3.0	2.9
Overall bleached yield, percent	36.0	44.0
Cuene I.V	4.5	4.6
Brightness, ELB	93.6	93.6
Viscose:		
Solution	7.5/6.5/34	9.0/5.5/28
Viscosity, b.f.s	35.0	35.9
Plugging value, g./cm.^{2}	1,050	2,400

[a] No wash.

From these tabulated results, it should be particularly noted than an 8.0 percent absolute increase (or a 22% relative increase) in overall yield of bleached pulp (based on the weight of wood used) is achieved employing the process of the present invention as applied to a paper grade sulfite pulp in comparison with the conventional prior art process applied to a conventional dissolving grade unbleached pulp. Additionally, the dissolving pulp produced by the present process possesses equivalent color properties as compared with the heretofore conventional dissolving pulp and has an improved plugging value.

The invention in its broader scope is not limited to the specific compositions, steps and processes described, and departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

We claim:

1. A process for producing dissolving pulps suitable for use in the manufacture of viscose rayon which comprises treating an unbleached sulfite pulp in a four-stage bleaching and refining process comprising in sequence (1) a chlorination stage wherein said sulfite pulp is treated with about 1–5 percent chlorine (ovendried pulp basis) for about 10–60 minutes, (2) a combined alkaline hypochlorite mild caustic extraction stage wherein at the conclusion of said hypochlorite treatment and without an intervening wash, said sulfite pulp is subjected to said caustic extraction at atmospheric pressure and at a temperature less than about 70° C. for a period of less than about 4 hours, (3) a cold caustic extraction stage at a temperature of about 15–50° C. under atmospheric pressure with sufficient caustic to remove hemicelluloses and other carbohydrate impurities from said pulp, and (4) an alkaline hypochlorite stage wherein an alkaline hypochlorite having about 2 percent available chlorine (based on the weight of the pulp) is added to the pulp

and the pH is maintained at least about 7 and the temperature at about 30–70° C.

2. The process of claim 1 wherein said unbleached sulfite pulp is a high yield, easy bleaching paper grade sulfite pulp.

3. The process of claim 2 wherein said paper grade sulfite pulp is prepared by a process comprising digesting wood chips in a soluble base cooking liquor having a total SO_2 content of about 6.0 to 8.5 percent and a combined SO_2 content of 0.8 to 1.2 percent, based on the weight of the liquor, for about 5 to 7 hours at about 130° to 150° C. and at a pH of 1 to 2.

4. The process of claim 2 wherein said paper grade sulfite pulp is prepared by a process comprising digesting wood chips in a cooking liquor having a total SO_2 content of about 3.5 to 5.0 percent and a combined SO_2 content of about 1.75 to 2.5 percent, based on the weight of the liquor, for about 5 to 7 hours at a pH of about 3 to 6 and a temperature of about 150° to 165° C.

5. The process of claim 1 wherein said combined alkaline hypochlorite-mild caustic extraction stage comprises treating said pulp with an alkaline hypochlorite at a pulp consistency of about 9–17% (oven dried pulp basis) in an amount sufficient to provide about 2–3 percent available chlorine (based on the weight of pulp) with excess caustic soda being incorporated to maintain the pH at about 10–11 when the hypochlorite is consumed, continuing the hypochlorite treatment of said pulp for a period of about 1–2 hours, at a temperature in the range of about 30–70° C., then without an intervening wash subjecting said pulp to a mild caustic extraction with an amount of sodium hydroxide sufficient to provide a final pH of about 10–11 and less than about 4 percent sodium hydroxide (based on the weight of pulp), at a temperature of up to about 70° C., and for a period of about 1–4 hours.

6. A process for bleaching and refining unbleached sulfite pulp which comprises treating said unbleached pulp in a chlorinatioin stage at a pulp consistency of about 3 percent (oven dried pulp basis) with about 1–5 percent chlorine (oven dried pulp basis) at a pH less than about 4.0 and at a temperature of about 5–30° C., about 10 to 60 minutes, washing the resulting pulp with water and subjecting the pulp to a combination hypochlorite-mild caustic extraction stage wherein an alkaline hypochlorite is added to the washed pulp suspension at a pulp consistency of about 9–17% (oven dried pulp basis) in an amount sufficient to provide about 2–3 percent available chlorine (based on the weight of the pulp) with excess caustic soda being incorporated to maintain the pH at about 10–11 when the hypochlorite is consumed, continuing this treatment until the hypochlorite is consumed at a temperature in the range of about 30–70° C., then without an intervening wash, subjecting the pulp stock to a mild caustic extraction with sufficient sodium hydroxide to insure an excess of caustic at the end of the treatment at a temperature of less than about 70° C. for a period of about 1–4 hours and a final pH of about 10–11, washing with water and dewatering the resulting pulp and then subjecting said pulp to cold caustic extraction stage with aqueous caustic soda solution at a temperature in the range of about 15–50° C. under atmospheric pressure with caustic concentration of about 4–11% (on a solution basis) and a consistency of about 3% (based on the weight of the pulp), for about 3–20 minutes, washing and dewatering the cold caustic extracted pulp and adding an alkaline hypochlorite solution having about 2% available chlorine (based on the weight of the pulp) to the pulp with a sufficient amount of sodium hydroxide also being added to maintain a pH of at least about 7 at a pulp consistency of about 9–17% and a temperature of about 30°–70° C. and then recovering the resulting bleached and refined viscose grade dissolving pulp.

7. The process of claim 6 wherein said hypochlorite treatment in said combination hypochlorite-mild caustic extraction stage is carried out for a period of about 1–2 hours.

8. The process of claim 6 wherein said mild caustic extraction in said combination hypochlorite-mild caustic extraction stage is carried out at atmospheric pressure with the addition of an amount of sodium hydroxide sufficient to provide a final pH of about 10–11 and less than about 4 percent sodium hydroxide (based on the weight of the pulp).

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