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PULPING OF WOOD WITH SULFITE BASE DIGESTION LIQUOR CONTAINING ACETIC ACID

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ABSTRACT OF THE DISCLOSURE

A high-grade sulfite wood pulp of substantially increased bleachability and intrinsic viscosity is produced by digesting wood in a conventional manner with a soluble-base sulfite digestion liquor in which from about 20 to 75 percent of the water, by volume, has been replaced with acetic acid.

BACKGROUND OF THE INVENTION

The well-known and widely used sulfite pulping process for the production of refined cellulose fiber suitable for high-grade paper stock and suitable for dissolving or for chemical pulp uses involves digesting wood (preferably in the form of chips) in an aqueous sulfite digestion liquor at elevated temperatures and pressures to solubilize and remove lignin and other unwanted materials from the cellulose. The substantially lignin-free cellulosic fiber that results is then removed from the digestion liquor and subjected to various stages of purification (i.e., bleaching) and washing to remove remaining small amounts of lignin and other impurities and then dried. Very white, active pulps of substantially pure cellulose fiber are produced in this manner.

Sulfite digestion and subsequent bleaching of the wood, however, not only remove lignin and impurities, they also attack and degrade or depolymerize the cellulose itself, more or less directly in proportion to their severity. This is, and has to be acceptable to a degree, but on the whole, the art diligently seeks to obtain the highest yield possible of the least degraded (highest I.V.) chemical cellulose having maximum purity and whiteness. Research is constantly going on in an effort to develop improved methods of sulfite pulping that will either yield less degraded (higher I.V.) unbleached pulp of a given easy bleachability or an easier bleaching pulp of a given relatively high I.V. Either object obviously would lead to a final bleached cellulose having a maximum I.V. and whiteness.

As noted above, bleachability of an unbleached pulp is customarily measured by means of the well-known standard TAPPI potassium permanganate number (K No.). Other factors being equal, decreasing K Nos. indicate an increasing ease of bleaching. Degradation or depolymerization of the cellulose in the pulp, on the other hand, is usually measured by determination of the intrinsic viscosity (I.V.) of its solution in a standardized cuene solution. A decreasing I.V. is indicative of increased degradation or depolymerization of the cellulose and as a rule K No. can only be lowered at the expense of reduction of the I.V. Therefore, as one measure of the quality of an unbleached sulfite pulp we have become accustomed to determining the ratio of the K No./I.V. and, other factors remaining equal, the lower the numerical value of the ratio, the better the pulp. Applying this standard to conventional sulfite dissolving pulps we find that they normally exceed a value of 1.0 and in many cases they exceed 1.5. One common use for sulfite dissolving pulps is the production of cellulose acetate. It is well-known that acetylation-grade pulps should have as low a hemicellulose content as possible, the hemicellulose

content being an important criterion in evaluation of the quality of said pulps. Glucomannans are one type of hemicellulose that invariably carries over from the wood to appear at least in trace quantities in most dissolving woodpulps. In the course of an investigation, the objective of which was to discover a way to promote the hydrolytic cleavage of glucomannan molecules during the sulfite digestion of wood and thereby facilitate their removal, I carried out certain experiments in which various amounts of acetic acid replaced some of the water in the sulfite digestion liquors used. To my surprise, not only did the addition of the acetic acid lower the glucomannan content of the resultant pulp, but most unexpectedly, when the acetic acid content of the liquor was within certain limits the K No. of the pulp was significantly decreased without any compensating decrease in the I.V. In fact, the I.V. of the pulp was even higher than normal. On further investigation, I found that by cooking the wood with a soluble-base sulfite digestion liquor containing controlled amounts of acetic acid, I could readily obtain pulps having a K No./I.V. ratio significantly below 1.0 and even below 0.5 under the proper conditions, if desired.

SUMMARY OF THE INVENTION

I have devised an improved process for producing easy-bleaching sulfite woodpulp having a significantly increased I.V. value. In the process of my invention, wood (preferably in the form of conventional chips) is digested in the usual manner with an aqueous soluble-base sulfite digestion liquor containing from about 20 to 75 percent by volume (preferably about 50 percent) of acetic acid in place of an equivalent amount of the water normally present in the digestion liquor. This modification of the digestion process will produce an unbleached pulp suitable for use in the production of high-grade paper or as an improved dissolving or chemical-grade cellulose which has a significantly higher than normal I.V. and a controllable K No./I.V. ratio of 1.0 or below. The mannan content of the pulp is also reduced.

DETAILED DESCRIPTION

Commercial sulfite pulping practice involves digesting or cooking wood (usually in the form of chips) in an aqueous sulfite digestion liquor at temperatures ranging from about 125 to 150° C., and pressures of from about 50 to 150 p.s.i.g. for from about 3.5 to 9.0 hours. A pulp is produced comprising essentially pure cellulose and a spent liquor containing lignin, soluble carbohydrates, inorganic salts and other soluble or solubilized constituents of the wood. The liberated cellulose fiber is then separated from the spent sulfite liquor and purified by various combinations of bleaching, extraction, and washing, and finally dried. The result is a reactive, very white, relatively pure cellulose fiber suitable for conversion into high-grade papers and for use in the production of regenerated cellulose and cellulose derivatives such as rayons, cellulose acetates, nitrates, etc.

The improved process of my invention and the product obtained thereby are based upon my discovery that when about 20 to 75 percent (by volume) of the water in the soluble-base sulfite digestion liquor is replaced by an equal amount of acetic acid, the digestion results in an easy bleaching pulp with an exceptionally high I.V., or conversely a pulp with an exceptionally low K No. for a given I.V. The replacement of less than about 20 percent of the water content of the digestion liquor with acetic acid will produce some reduction in the K No./I.V. ratio of the unbleached pulp; however, there is a dramatic and most unexpected reduction in said ratio when the acetic acid is increased above 20 percent. Similarly, some reduction of the K No./I.V. ratio is still obtained at acetic acid replacements in excess of 75 percent by volume, but additions of acetic acid much in excess of this amount are accompanied by adverse effects on products produced therefrom such as the haze and color of cellulose acetate films and also the beneficial effects are reduced drastically.

The conditions under which the practice of the invention are most advantageously carried out are essentially the same as those employed in conventional sulfite cooking practices. If a finished bleached product is desired having the same I.V. as a conventional pulp, a compensating increase in the severity of the cooking conditions is required which in turn results in a whiter and purer cellulose end product. The length of time, temperature and pressure of a cooking procedure required to obtain a pulp of a specified I.V. and/or K No. are variables that must always be taken into consideration in sulfite cooking operations and the determination of the cooking conditions best adapted to produce a product with desired characteristics in the practice of my invention in a matter well within the skill of workers in this art.

The following examples are illustrative, but not limitative of the practice of my invention.

EXAMPLE 1

Five cooks were made on southern pine chips each using 3.2 kilograms of wood on an oven dry basis in 12 liters of soda base sulfite digestion liquor containing the amounts of acetic acid and under the digestion conditions set out in Table I. The characteristics of the unbleached pulps obtained illustrate the striking increase in bleachability and I.V. afforded by the presence of the indicated percentages of acetic acid (glacial) in the digestion liquors.

TABLE I

	Cook No.				
	1	2	3	4	5
Digestion liquor:					
Acetic acid, percent by volume	0	5	25	50	97
Total SO_2, g./100 ml	6.15	6.13	6.13	6.10	6.10
Free SO_2, g./100 ml	5.43	5.41	5.41	5.38	5.38
Cooking schedule:					
Maximum temp., ° C	134	134	139	142	144
Maximum pressure, p.s.i.g	105	110	112	109	120
Total time, hrs.: mins	6:45	7:12	6:47	7:00	9:03
Pulp (unbleached):					
Screened yield percent	46.3	44.2	44.9	43.9	54.3
Tappi K No	18.1	12.5	8.2	5.5	31.6
Cuene I.V. ratio	9.89	11.02	12.02	11.18	13.45
K No./I.V. ratio	1.83	1.12	0.68	0.49	2.35
Mannan percent	7.2	7.2	6.7	4.8	------

EXAMPLE 2

Five portions of a batch of western hemlock wood chips each weighing 2.5 kilograms (oven dry basis) were cooked in 12 liter portions of soda base sulfite digestion liquor containing varying amounts of acetic acid under the conditions and with the results set out in Table II below:

TABLE II

	Cook No.				
	1	2	3	4	5
Digestion liquor:					
Acetic acid, percent by volume	0	5	25	50	ca.97
Total SO_2, g./100 ml	6.76	6.77	6.69	6.75	6.75
Free SO_2, g./100 ml	6.07	6.10	6.02	6.07	6.07
Cooking Schedule:					
Maximum temp., °C	139	139	143	145	150
Maximum pressure p.s.i.g	110	110	110	111	105
Total time, hrs. mins	5:33	5:32	6:27	6:30	11:50
Pulp (unbleached):					
Screened yield percent	50.5	49.5	45.4	49.0	49.0
Tappi K No	16.1	13.6	6.2	8.5	13.4
Cuene I.V	10.50	10.33	11.29	10.66	15.37
K No./I.V. ratio	1.53	1.31	0.55	0.80	0.87
Mannan, percent	9.0	9.2	7.8	4.8	9.1

EXAMPLE 3

Samples of unbleached pulps produced in Examples 1 and 2 from southern pine and western hemlock wood chips were bleached by a conventional bleaching process and then acetylated to triacetates by a conventional method. Comparative color and haze density determinations were then run on the acetate solutions thus formed by methods developed at Tennessee Eastman Corporation, with the results listed in Table III.

TABLE III

	Acetic acid in cooking liquor by volume percent		
	0	50	ca. 97
Southern pine pulp:			
Haze, p.p.m	150	45	150+
Color, p.p.m	570	580	650
Hemlock pulp:			
Haze, p.p.m	95	55	150+
Color, p.p.m	480	350	650

The use of acetic acid in the cooking liquor at the 50 percent level in the modified sulfite pulping process of the invention substantially lowers the triacetate haze levels. The color level improvement obtained in the triacetate solution prepared from hemlock pulp of the invention, however, did not appear in the southern pine pulp equivalent. It is evident, however, that the use of high concentrations of acetic acid such as 97 percent when cooking the wood by the process of the invention is detrimental to both the color and haze densities of triacetates prepared therefrom.

EXAMPLE 4

In a second series of cooks using the process and the same chips as in Example 2, a slight variation in the digestion time at a concentration of 50 percent by volume of acetic acid was made to illustrate how the I.V. ad the K No./I.V. ratio of the unbleached pulp could be varied. From the range of results obtained it is clear that considerable control of the characteristics of the product is easily obtained.

TABLE IV

	Cook No.			
	1	2	3	4
Acetic acid, percent by volume	0	50	50	70
Free SO_2, g./100 ml	6.06	6.10	6.32	6.11
Combined SO_2, g./100 ml	3.20	3.34	3.31	3 33
Cooking schedule:				
Maximum temp., °C	138	145	145	148
Total time, hrs.: m ns	5:16	6:20	7:40	8:30
Pulp (unbleached):				
Tappi K No	16.2	13.9	4.9	7.1
Cuene I. V	11.2	15.3	12.2	13.8
K No./I. V. ratio	1.40	0.91	0.40	0.51

EXAMPLE 5

The improvements in bleachability and I.V. resulting from the presence of acetic acid in the cooking liquor are substantial when using soluble-base sulfite liquors. These improvements, however, do not carry over, or at least are substantially less when cooking with a calcium-base sulfite liquor. This example illustrates this phenomena, the exact reason for which is not known.

A large uniform sample of hemlock wood chips was prepared and six experimental cooks made thereon using 2.5 kilogram portions on a dry weight basis and the process of Example 2. The acetic acid contents of the liquors, the digestion conditions and the results obtained are set out in Table V. It will be noted that substantial improvement in results was obtained only for the soluble-base sodium and ammonium-base sulfite liquors.

TABLE V

	Cook No.					
	1	2	3	4	5	6
Digestion liquor:						
Base	Na	Na	NH_3	NH_3	Ca	Ca
Acetic acid, percent by volume	0	50	0	50	0	50
Cooking schedule:						
Maximum temp. ° C	138	145	140	145	140	145
Maximum pressure p.s.i.g	110	110	110	110	110	110
Total time, hrs.: mins	5:16	7:40	5:12	6:30	6:08	7:00
Pulp (unbleached):						
Screened yield percent	47.7	46.4	44.8	43.7	45.1	44.3
Tappi K No	16.2	4.9	11.9	8.7	12.3	10.8
Cuene I.V	11.6	12.2	10.8	11.6	10.5	10.2
K No./I.V. ratio	1.40	0.40	1.10	0.75	1.17	1.06

From the data presented in the foregoing examples, it is apparent that the substitution of from about 20 to 75, and preferably about 50, percent by volume of acetic acid for the equivalent volume of water normally present in sulfite digestion liquors lowers the permanganate number of the unbleached pulp or in other words increases it bleachability. At the same time, unbleached I.V. values increase despite increases in cooking time and temperature. As a result, remarkably low K No./I.V. values are obtained. Moreover, it is also apparent that the mannan content of the pulp is lowered substantially by the use of up to about 50 percent acetic acid in the digestion liquor.

I claim:

1. In the process of pulping wood in aqueous soluble-base sulfite digestion liquor at elevated temperature and pressure, the improvement which comprises replacing from 20 to 75 percent by volume of the water in the digestion liquor with an equal volume of acetic acid, thereby producing a substantially less degraded unbleached pulp of increased average degree of polymerization as measured by its intrinsic viscosity and increased ease of bleaching as measured by its potassium permanganate number.

2. The process according to claim **1** in which the sulfite digestion liquor contains about 50 percent by volume acetic acid based on the volume of water normally present in said liquor.

3. The process according to claim **1** in which the unbleached pulp obtained by digesting the wood chips with said acetic acid-containing digestion liquor has a K No./I.V. ratio no greater than one.

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