

1

3,354,030

ALKALINE SULFITE DIGESTION FOLLOWED BY ACID DIGESTION WITH BISULFITE

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This invention pertains to a multistage pulping process for the preparation of a very clean essentially whole fibered ultra high yield pulp. More specifically, this invention pertains to a pulping process comprising at least two separate and distinct stages of treating cellulosic material for the realization in high yields of a pulp having a high brightness coefficient.

The respective advantages of conventional sulfite and alkaline digestion processes are well known. In either process, all of the constituents of the wood are simultaneously attacked to different degrees during digestion. The net result is that some of the non-cellulosic materials, e.g. lignin and hemicelluloses, remain in the pulp while at the same time the cellulose itself has been subjected to some attack. This is especially true of the alkaline process in that the hemicelluloses, which are comprised mainly of the polyuronides, are dissolved at a much faster rate than the lignin in the early stages of the process. As the digestion process proceeds, the polyuronides content diminishes to the extent that its rate of removal gradually becomes slower than the rate of lignin removed. It is understood of course that the percentage of lignin in the pulp is also continually diminishing. These conditions continue until nearly all of the lignin originally present between the fibers has been essentially removed. If an attempt is made to reduce the lignin content further by dissolving the fiber-wall lignin, which lignin dissolves at a much slower rate, it will be observed that the cellulans and the celluloses are severely attacked and hence dissolve at just about the same rate as the fiber-wall lignin.

On the other hand, in sulfite pulping both the inter-fiber and the fiber-wall lignin are simultaneously dissolved. Hence, all things being equal, it is possible to produce a pulp having less lignin content and requiring less bleaching in order to end up with a comparable pulp. However, the sulfite process is characterized by unfavorable side reactions which destroy the cooking liquor. Additionally, pulp produced by this method is generally weaker than that produced by the alkaline process. Moreover, a serious drawback of the sulfite process is that it is not attractive for the pulping of all types of wood. Whereas, the alkaline process is suitable for all types of wood and does produce a stronger pulp, especially before bleaching which is sometimes employed since the pulp produced by this method tends to be darker. It is to be noted however, that subsequent bleaching of the pulp may weaken it. To offset this effect as well as to minimize the cost of expensive bleaching chemicals, the art has resorted to more stringent cooking conditions in the alkaline process. This has not totally relieved the problems associated with achieving a clean pulp of high yield because these conditions result in alkaline hydrolysis and subsequent degradation of the cellulosic material undergoing treatment.

To offset the disadvantages of either process, various multistage processes which incorporate or combine attractive features of these processes have been proposed and attempted heretofore. For example, in Swedish Patents 77,429 and 79,840, a process for producing sulfite cellulose by precooking with alkali sulfite solution and finally cooking with a liquor which contains free sul-

2

furous acid is disclosed. The object in those patents is to first sulfonate the lignin without having any acid or alkaline hydrolysis occur and then to bring about an acid hydrolysis, after which the cellulose is split off from the lignin and a pulp of a sulfite type is obtained. As brought out in the Swedish Patent 79,840, other multistage processes have been attempted, such as an initial harsh alkaline stage followed by an acid stage. Other attempts include a combination of two alkaline stages as well as varying the cooking temperatures and pressures, for example see U.S. Patent 2,885,317 which teaches the use of hydraulic over-pressures as high as possible. In general, such multistage processes are characterized by a harsh alkaline treatment, acid treatment, and/or both as well as elaborate and rigid processing conditions. Thus, a multistage process whereby a very clean pulp can be produced in a very high yield by a process which is milder, simpler, and more expeditious would be a welcome contribution to the art.

An object of this invention is to provide a process whereby a very clean whole fibered pulp is realized.

Another object is to provide a process for the preparation of high yield pulp.

Yet another object is to provide a multistage process characterized by its simplicity and mildness whereby a pulp having a high brightness coefficient is produced in high yields. These and further objects will come to light as the discussion proceeds.

A very bright essentially whole fibered ultra high yield pulp is provided pursuant to the practice of this invention by a multistage process which comprises treating wood chips at least once, each time with an initially alkaline liquor at an elevated temperature and pressure and after each digestion blowing the digester and effecting separation between the treated chips and the liquor, and thereafter digesting the treated cellulosic material at least once, each time with an initially acidic liquor at an elevated temperature and pressure and after each digestion blowing the digester and effecting separation between the treated cellulosic material and the liquor. By blowing is meant that the treated chips or cellulosic material is literally blown from the treating zone or digester so that the treating liquor which has penetrated the wood chips immediately flashes and thus defibers them. Thus, it can be seen that by multistage is meant a first alkaline treatment stage and thereafter a second stage comprising an acid treatment. It is especially preferred to wash the wood chips after termination of treatment in the first stage, that is after alkaline treatment, with clear water. The first stage cooking or alkaline treatment is generally conducted at a pH of about 8 or greater, whereas the second stage cooking or acid treatment, at a pH within the range of from about 4.3 to about 6.9.

The process of this invention can be conducted on a batchwise or continuous basis. By batchwise is meant that the wood chips can be treated in a first digester whereafter they are blown to a blow tank and then passed into a drainer and finally to another digester for subsequent treatment. A continuous process would comprise for example, a series of B-K reaction chambers (see page 454 of Pulp and Paper Manufacture Vol. 1—Preparation and Treatment of Wood Pulp, McGraw-Hill, 1951) through which the wood chips would be continually processed. It is to be noted that the pulp produced by way of this invention being a very clean whole fibered material does not require as much subsequent mechanical treatment as pulp produced by conventional processes. Thus, this invention also provides a continuous multistage process for the production of fibrous cellulosic pulp which comprises, in the sequence specified:

(1) treating wood chips in a plurality of treating zones,

each time with an initially alkaline liquor at an elevated temperature and pressure and after each treatment discharging the contents from the treating zone and effecting separation between the treated chips and the liquor, and

- (2) thereafter treating the resultant cellulosic material in a plurality of treating zones, each time with an initially acidic liquor at an elevated temperature and pressure and after each treatment discharging the contents from the treating zone and effecting separation between the treated cellulosic material and the liquor.

The temperatures to be employed in the practice of this invention should be at least about 280° F., and generally no more than 400° F. Suitable pressures are those equivalent to the steam pressure of the cooking liquor which is at least around 50 p.s.i.a. as based upon a temperature of about 280° F. For the first stage cooking, a preferred temperature range is from about 320° F. to about 340° F., especially when employing the most preferred cooking liquor which comprises sodium sulfite buffered with sodium carbonate so as to have an initial pH of from about 10.5 to about 11.0. A preferred temperature range for the second cooking stage or acid treatment, is within the range of from about 320° F. to about 360° F., especially when employing the most preferred acid cooking liquor which comprises sodium bisulfite which may be buffered with sodium bicarbonate so as to have an initial pH of from about 4.3 or more. As brought out above, suitable pressures are those equivalent to the steam pressure of the cooking liquor. Hence, it follows that a preferred pressure range for the first stage is from about 90 to about 120 p.s.i.a. and for the second stage, of about 90 to about 150 p.s.i.a.

The cooking times to be employed, that is the hold period for any one treatment step, need not exceed 60 minutes, however generally being more than 10 minutes. An especially preferred time range is from about 10 to about 30 minutes. It is understood of course that as the operating temperatures are increased as well as the pH of the cooking liquor, then the cooking time can be decreased commensurably without departing from the spirit of this invention.

The total number of treating steps for both stages seldom exceeds a total of 6 cooks, preferably 1 alkaline cook and 1 acid cook, viz. 2 cooks altogether, especially when employing hard woods as the raw material.

The liquid to wood ratio should preferably be at least 3:1 respectively. An even more preferred ratio is from about 5 or 6:1, especially when practicing the process of this invention on a continuous basis.

The process of this invention is particularly attractive for pulping broadleaf woods or hard woods, e.g. birch, beech, maple, poplar, oak, gum, or the like since the highest yields in the minimum amount of time are achieved when employing these raw materials. However, coniferous or soft woods can also be easily pulped and enhanced by way of the instant invention, e.g. fir, spruce, cedar, pine, hemlock, or the like. Such woods generally have a higher lignin content and when employed as the raw material in the process of this invention it is preferred to conduct the first stage or alkaline treatment at a slightly greater pH value, at higher temperatures, with longer times, with more stages, or using any suitable combination of these. In short, any conventional debarked wood is suitable as a raw material. It is to be understood of course that the processing conditions will vary slightly depending upon the type of wood employed as a feed stock. Generally speaking, to maximize yields it will only be necessary to correlate the temperature, time, and pH of the cooking liquor for a given type of wood.

The following data demonstrates several distinct benefits of the instant invention, namely that the essentially whole fibered pulp produced by the way of this invention has a combined brightness coefficient and strength cou-

pled with higher yields than that obtainable by prior art techniques, whether single stage or multistage processes.

5	Pulp by Process Shown (Hardwood)	Yield, Percent	Hunter Brightness, Percent	Tensile Strength, Percent at 450-500 CS Freeness
10	Conventional Alkaline—Cold			
	Caustic.....	88	40	12
	Conventional Sulfite or Kraft.....	48	26	60
	This Process.....	79	40	42

As can be seen from the above, a yield and brightness equaling that of a conventional alkaline process is realized yet at significantly greater tensile strength, viz. that approaching a conventional sulfite process.

The following examples are presented wherein all parts are by weight unless otherwise specified.

EXAMPLE I

MIXED HARDWOODS (GUM AND OAK)

Alkaline stage

Step 1.—The mixed hardwood chips were charged to a digester along with sufficient liquor to have a liquor to wood ratio of 6:1. The cooking liquor comprised 12 percent Na_2SO_3 and 6 percent NaHCO_3 based upon oven dry wood. The initial pH of the cooking liquor was 8.8. The digester was closed and the contents heated for 30 minutes until a temperature of 335° F. was attained. The contents were heated for an additional 45 minutes at this temperature. Thereafter the treated chips were blown from the digester at a pressure of 95 p.s.i.a. The final pH of the cooking liquor was 7.9.

Step 2.—The treated chips were washed with clear water.

Acid stage

Step 3.—The treated chips were then charged into a digester and sufficient cooking liquor added to make up a 5:1 liquor to wood ratio. The cooking liquor comprised a 12 percent NaHSO_3 solution based upon oven dry wood having an initial pH of 4.7. The digester was then closed and heated for 45 minutes until a temperature of 335° F. was attained at which point the temperature was held constant and the digester contents heated an additional 60 minutes. The treated pulp was then blown from the digester at a pressure of 95 p.s.i.a. The final pH of the cooking liquor was 7.0.

Results

	Percent
Yield	82.5
Lignin	10.3
Strength at 470 Canadian Standard Freeness	
	Percent
Tear	162
Tensile	39
Burst	66
Hunter brightness	about 38

EXAMPLE II

100% SYCAMORE

Alkaline stage

Step 1.—The wood chips were charged to a digester along with sufficient liquor to have a liquor to wood ratio of 5:1. The cooking liquor comprised 10 percent Na_2SO_3 and 5 percent Na_2CO_3 based upon oven dry wood. The initial pH of the cooking liquor was 10.8. The digester was closed and the contents heated for 30 minutes until a temperature of 340° F. was attained. The contents were heated for an additional 60 minutes at this temperature. Thereafter the treated chips were blown from the digester at a pressure of 100 p.s.i.a. The final pH of the cooking liquor was 6.1.

5

Step 2.—The treated chips were then washed with clear water.

Acid stage

Step 3.—The treated chips were then charged into a digester and sufficient cooking liquor added to make up a 5:1 liquor to wood ratio. The cooking liquor comprised a 10 percent NaHSO_3 solution based upon oven dry wood having an initial pH of 4.6. The digester was then closed and heated for 30 minutes until a temperature of 340° F. was attained at which point the temperature was held constant and the digester contents heated an additional 45 minutes. The treated pulp was then blown from the digester at a pressure of 100 p.s.i.a. The final pH of the cooking liquor was 4.9.

Results

	Percent
Yield	73.3
Lignin	12.7

Strength at Various Canadian Standard Freenesses

	630	465	265	160
Percent Tear.....	111	131	129	123
Percent Tensile.....	34	41	55	59
Percent Burst.....	42	64	81	95

Hunter Brightness: 36 percent.

EXAMPLE III

50% GUM-50% POPLAR

Alkaline stage

Step 1.—The wood chips were charged to a digester along with sufficient liquor to have a liquor to wood ratio of 5:1. The cooking liquor comprised 10 percent Na_2SO_3 and 5 percent Na_2CO_3 based upon oven dry wood. The initial pH of the cooking liquor was 10.7. The digester was closed and the contents heated for 90 minutes until a temperature of 340° F. was attained. The contents were heated for an additional 30 minutes at this temperature. Thereafter the treated chips were blown from the digester at a pressure of 100 p.s.i.a. The final pH of the cooking liquor was 7.5.

Step 2.—The treated chips were washed with clear water.

Acid stage

Step 3.—The treated chips were then charged into a digester and sufficient cooking liquor added to make up a 5:1 liquor to wood ratio. The cooking liquor comprised a 10 percent NaHSO_3 solution based upon oven dry wood having an initial pH of 4.6. The digester was then closed and heated for 60 minutes until a temperature of 340° F. was attained at which point the temperature was held constant and the digester contents heated an additional 20 minutes. The treated pulp was then blown from the digester at a pressure of 100 p.s.i.a. The final pH of the cooking liquor was 5.0.

Results

	Percent
Yield	71.0
Lignin	18.5

Strength at Various Canadian Standard Freenesses

	675	555	370	215
Percent Tear.....	133	139	145	135
Percent Tensile.....	30	41	50	54
Percent Burst.....	40	65	81	94

Hunter Brightness: 34 percent.

6

EXAMPLE IV

MIXED HARDWOODS (PRIMARILY
OAK AND GUM)

Alkaline stage

Step 1.—The mixed hardwood chips were charged to a digester along with sufficient liquor to have a liquor to wood ratio of 5:1. The cooking liquor comprised 10 percent Na_2SO_3 and 5 percent NaHCO_3 based upon oven dry wood. The initial pH of the cooking liquor was 8.3. The digester was closed and the contents heated 45 minutes until a temperature of 335° F. was attained. The contents were heated for an additional 105 minutes at this temperature. Thereafter the treated chips were blown from the digester.

Step 2.—The treated chips were washed with clear water.

Step 3.—The same procedure as employed in Step 1 was followed except the cooking liquor comprised a solution of 4 percent Na_2SO_3 and 2 percent NaHCO_3 based upon oven dry wood having a pH of 8.3. The total cooking cycle was 2 hours in duration with a 45 minute rise period to a temperature of 340° F.

Step 4.—The treated chips were again washed with clear water.

Acid stage

Step 5.—The treated chips were then charged into a digester and sufficient cooking liquor added to make up a 5:1 liquor to wood ratio. The cooking liquor comprised an 8 percent NaHSO_3 solution based upon oven dry wood having an initial pH of 4.3. The digester was then closed and heated for 45 minutes until a temperature of 340° F. was attained at which point the temperature was held constant and the digester contents heated an additional 105 minutes. The treated pulp was then blown from the digester.

Results

Percent yield: 87.

Strength at 540 Canadian Standard Freeness:

	Percent
Tear	218
Tensile	41
Burst	74
Hunter brightness	43

As brought out above, the first stage or alkaline treatment is conducted with a cooking liquor having a pH of at least 8. An especially preferred cooking liquor comprises an aqueous solution of sodium sulfite buffered with sodium carbonate and having a pH of from about 10.5 to about 11.0. Another preferred cooking liquor comprises sodium sulfite buffered with sodium bicarbonate and having a pH of from about 8.0 to about 8.5. Other sulfite cooking liquors, buffered or not, can readily be employed in lieu of the above, for example other suitable liquor bases are the sulfites and sulfides of lithium, potassium, rubidium, magnesium, calcium, strontium, barium, ammonium, and the like, as well as mixtures thereof.

For the second stage, an especially preferred cooking liquor is sodium bisulfite having an initial pH of from about 4.3 to about 5.0. Another preferred cooking liquor comprises sodium bisulfite buffered with sodium bicarbonate and having an initial pH of from about 6.0 to about 6.9. Generally speaking, the pH of the second stage cooking liquor is maintained within the range of from about 4.3 to about 6.9. As in the first stage, cooking liquors having bases other than sodium can likewise be employed here, for example, the bisulfites of lithium, potassium, rubidium, magnesium, calcium, strontium, barium, ammonium, and the like, as well as mixtures thereof.

What is claimed is:

1. A multistage pulping process for the production of

7

high yield pulp having a lignin content less than 20 percent by weight based upon the weight of the pulp comprising, in combination, the consecutive steps of,

(a) at least once alkali digesting, and then blowing from said alkali digesting, particles of fibrous cellulosic material, said alkali digesting being by contacting said particles of fibrous cellulosic material for a period of about 10 to about 60 minutes with an aqueous solution of a sulfite compound having an initial pH of about 8.0 to about 11.0 at a temperature of about 280° F. to about 400° F. and a pressure of about 50 to about 150 p.s.i.a., said aqueous solution of a sulfite compound being present in a volume sufficient to provide a solution to particles volume ratio of about 3 to 1 to about 6 to 1 and said sulfite compound being present in a concentration sufficient to provide at least about 5 percent by weight based upon the dry weight of said particles, and then

(b) at least once, acid digesting, and then blowing from said acid digesting, the alkali digested and blown particles of fibrous cellulosic material to recover said high yield pulp, said acid digesting being by contacting said alkali digested and blown particles of fibrous cellulosic material for a period of about 10 to about 60 minutes with an aqueous solution of a bisulfite compound having an initial pH of about 4.3 to about 6.9 at a temperature of about 280° F. to about 400° F. and a pressure of about 50 to about 150 p.s.i.a., said aqueous solution of a bisulfite compound being present in a volume sufficient to provide a solution to particles volume ratio of about 3 to 1 to about 6 to 1 and said bisulfite compound being present in a concentration sufficient to provide at least about 5 percent by weight based upon the dry weight of said particles.

2. The process of claim 1 further characterized by said sulfite compound being at least one of the group consisting of the sulfites of sodium, lithium, potassium,

8

rubidium, magnesium, calcium, strontium, barium and ammonium; materials which will form the preceding said sulfites in aqueous solution; and mixtures thereof.

3. The process of claim 1 further characterized by said bisulfite compound being at least one of the group consisting of bisulfites of sodium, lithium, potassium, rubidium, magnesium, calcium, strontium, barium, ammonium; materials which will form the preceding said bisulfites in aqueous solution; and mixtures thereof.

4. The process of claim 1 further characterized by said sulfite compound being sodium sulfite.

5. The process of claim 1 further characterized by said bisulfite compound being sodium bisulfite.

6. The process of claim 4 further characterized by said aqueous solution of sodium sulfite being buffered with a buffering agent.

7. The process of claim 5 further characterized by said aqueous solution of sodium bisulfite being buffered with a buffering agent.

8. The process of claim 1 further characterized by said alkali digested and blown particles of fibrous cellulosic material being water-washed before being subjected to step (b).

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