United States Patent

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Continuation-in-part of application Ser. No. 539,683, Apr. 4, 1966, now Patent No. 3,479,249.
The portion of the term of the patent subsequent to Nov. 18, 1986, has been disclaimed.

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[54] **TREATMENT OF WOODPULP WITH AN ALKALINE SOLUTION CONTAINING FORMALDEHYDE PRIOR TO A BISULFITE COOKING THEREOF**
8 Claims, 5 Drawing Figs.

[52] **U.S. Cl.** **162/72,** 162/83, 162/84, 162/86

[51] **Int. Cl.** **D21c 3/20**

[50] **Field of Search** 162/9, 17, 18, 24, 25, 26, 32, 72, 83, 84, 86, 165, 166, 180

[56] **References Cited**

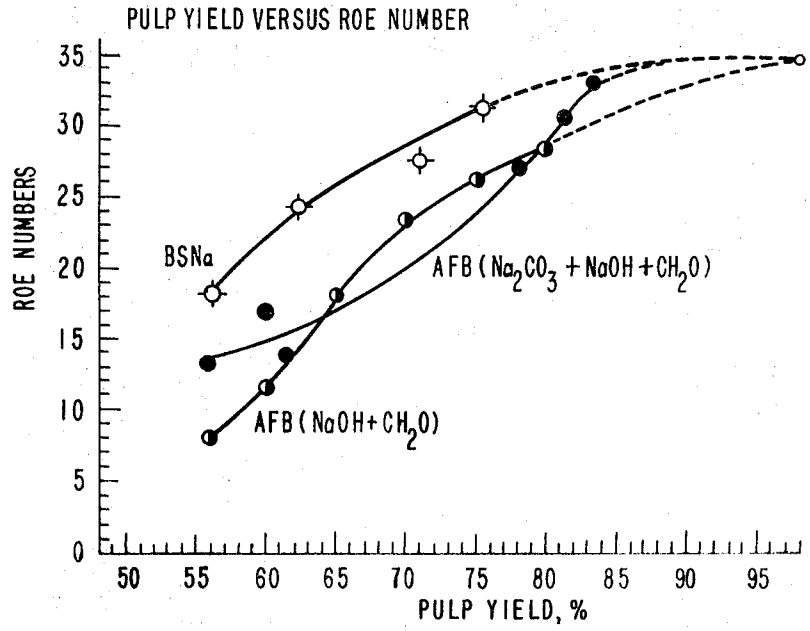
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ABSTRACT: A bisulfite wood-pulping process in which not more than about 2 percent by weight, based on the wood, of formaldehyde in an alkaline solution is used to pretreat the wood prior to the bisulfite cooking.

FIG. 1



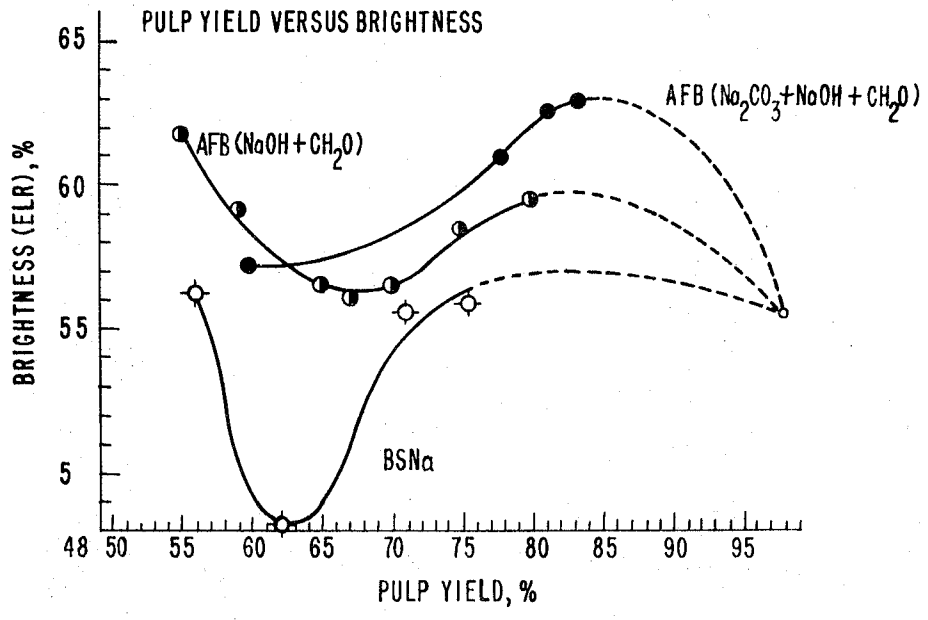


FIG. 2

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FIG. 3

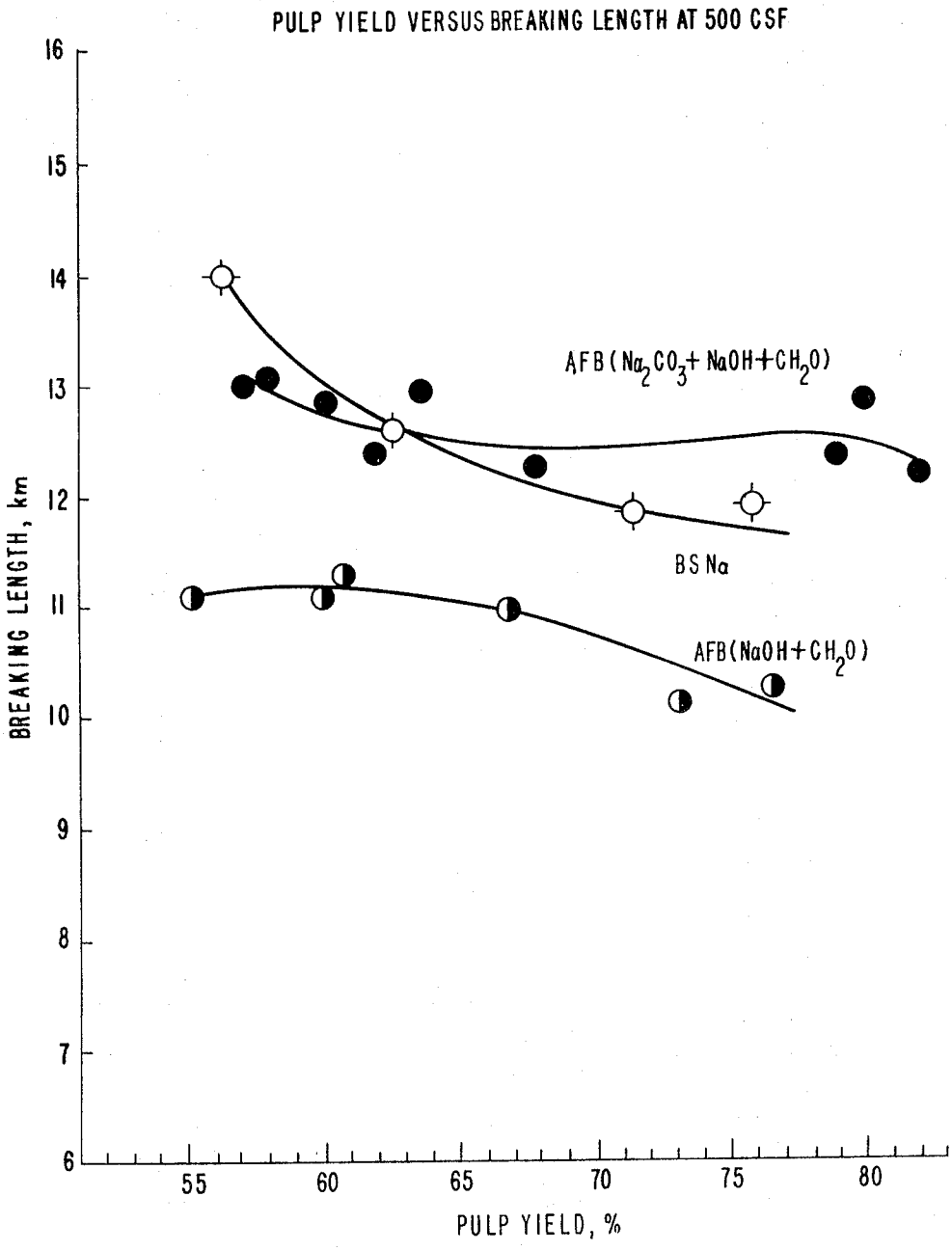

PULP YIELD VERSUS BREAKING LENGTH AT 500 CSF
BREAKING LENGTH, km
PULP YIELD, %
16
15
14
13
12
11
10
9
8
7
6
55
60
65
70
75
80
AFB (Na2CO3 + NaOH + CH2O)
BS Na
AFB (NaOH + CH2O)

FIG. 4

PULP DATA	COOKING PROCESS									
	A.F.B.									
	A		B		C		D		E	
TOTAL COOKING TIME, HOURS	12:20		9		8		8½		6	
SCREENED YIELD, % O.W.	51.4		58.3		59.7		60.5		-----	
SCREENINGS, % O.W.	0.7		0.75		1.2		2.0		-----	
TOTAL YIELD, %	52.1		59.05		60.9		62.05		76.03*	
BRIGHTNESS (ELREPHO) %	63.7		62.0		59.7		58.5		60.2	
ROE NUMBER	6.3		9.4		9.4		12.1		27.0	
K#	23		40.6		48.7		68.3		122	
VISCOSITY, TAPPI 230 Sm50, cp	28.8		32.6		27.7		21.3		N.D.	
ALPHA CELLULOSE, %	85.9		86.2		87.0		86.9		88.3	
PENTOSAN, %	5.0		5.1		5.3		5.1		4.8	
MANNAN, %	16.5		13.3		13.9		14.4		15.9	
XYLAN, %	4.8		4.3		4.2		4.5		5.3	
RESIN, %	0.47		0.5		0.4		0.5		0.57	
LIGNIN, %	2.0		3.6		6.7		7.8		17.7	
STRENGTH AT CSF, ml :	500	300	500	300	500	300	500	300	500	300
MULLEN, % PTS/LB	133	140	133	141	138	145	132	138	128	131
BREAKING LENGTH, m.	11,200	11,100	10.900	11,300	11,100	11,600	11,300	11,800	10,300	10,800
TEAR FACTOR	71	61	64	61	63	59	63	57	61	58
FOLD (SCHOPPER)	500	470	350	330	340	400	340	400	186	209
OPACITY, %	63.8	56.6	62	59	61.0	56.5	68	62.7	69.0	66.0

*OBTAINED BY DISC REFINING OF WHOLE COOK.

FIG. 5

PULP DATA	COOKING PROCESS: CONVENTIONAL Na-BASE BISULFITE, pH4 (8S Na)							
	F		G		H		I	
TOTAL COOKING TIME, HOURS			7:30				6:55	
SCREENED YIELD, % O.W.	-----		---------		---------		---------	
SCREENINGS, % O.W.	-----		---------		---------		---------	
TOTEL YIELD, %	49.3*		60.6*		70.0*		74.6*	
BRIGHTNESS (ELREPHO) %	50.6		54.7		54.3		54.7	
ROE NUMBER	8.4		17.5		27.6		28.8	
K#	40		85		125		130	
VISCOSITY, TAPPI 230 Sm50, cP	22.3		---------		---------		--------	
ALPHA CELLULOSE, %	-----		88.6		87.6		88.5	
PENTOSAN, %	4.4		5.18		4.79		5.18	
MANNAN, %	-----		--------		--------		--------	
XYLAN, %			--------		--------		--------	
RESIN, %	0.59		0.63		0.56		0.45	
LIGNIN, %	10.1		--------		19.6		21.5	
STRENGTH AT CSF, ml:	391	300	378		500	300	500	300
MULLEN, % PTS/LB	146	158	139		132	144	130	136
BREAKING LENGTH, m	12,328	12,900	---	11,508	10,700	11,600	10,400	10,800
TEAR FACTOR	65	66		69	69	62	67	60
FOLD (SCHOPPER)	514	570		383	270	280	240	230
OPACITY, %	62.9	60.5		66.6	70	64	70	70

*OBTAINED BY DISC REFINING OF WHOLE COOK.

TREATMENT OF WOODPULP WITH AN ALKALINE SOLUTION CONTAINING FORMALDEHYDE PRIOR TO A BISULFITE COOKING THEREOF

This application is a continuation-in-part of copending U.S. Ser. No. 539,683, filed Apr. 4, 1966 now issued to U.S. Pat. No. 3,479,349.

That patent relates to a wood-pulping process for making paper pulps of improved unbleached brightness, increased yield, and other improved pulp characteristics. More particularly, it relates to the use of an alkaline solution containing a low concentration of formaldehyde before cooking wood by the sulfite process. The use of this process is highly advantageous for coniferous woods and, particularly, for woods such as pines in which the polyphenolic components interfere with normal pulping by the sulfite process. The sulfite process is discussed at length in, for instance, Calkin, J.B.; *Modern Pulp and Paper Making:* (3rd Ed.) Reinhold Publishing Corporation; New York, 1957; p. 81 et. seq.

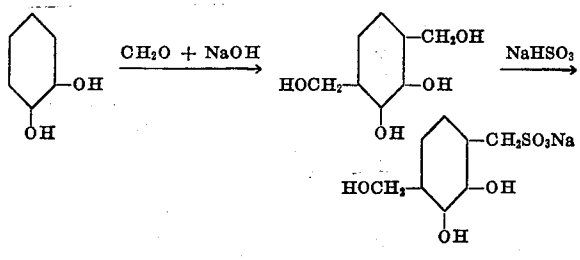
Many attempts have been made in the past to arrive at a satisfactory process for pulping of pines by the sulfite process. The use of soluble bases such as sodium, magnesium, and ammonium has led to substantial improvements over calcium base booking. Pine chips from young trees can be successfully cooked by the conventional calcium base sulfite process, but difficulties increase with the age of the tree. The need to harvest relatively older trees from slower growing northern pines in contrast to fast-growing southern pine indicates the problem.

It has been shown that the heartwood portion of pines is responsible for their more difficult pulping characteristics; sapwood, on the other hand, pulps satisfactorily with any base by the sulfite process. Consequently, the relatively high proportion of heartwood in slow-growing trees of normal age for harvesting eliminates the use of calcium base in conventional sulfite cooking.

However, even the use of a soluble base in pulping of pines will result in pulp characteristics inferior to those of spruce and other coniferous woods of relatively low resin content. This is particularly apparent with reference to delignification (yield at comparable Roe number) and unbleached pulp brightness.

Hägglund (Cellulose Chemie 8 (No. 3 25 (1927)) and more recently Erdtmann (Tappi 23, 303 (1949)) have shown that an ether-, benzene-insoluble, but alcohol- or acetone-soluble compound contained in the heartwood of pines interferes with normal delignification in lime base sulfite cooking. Such compounds were identified by Erdtmann as resorcinollike polyphenols such as pinosylvin, pinosylvin methyl ether, and flavanones which amount to about 20 percent of the total resin of pine or to approximately 1 percent of the heartwood portion of pine. Polyphenols condense easily with lignin at higher temperature. As a result, large lignin-polyphenol complexes are formed with simultaneous blocking of active groups which are needed for sulfonation and final solubilization of the lignin.

Blocking of the reactive position of the polyphenol prior to the start of the sulfite cook is needed to prevent condensation with lignin. Experiments by Alder and Stockman (Svensk Papperst. 54,477 (1951)) with phenolic model compounds (catechol) indicated that such a reaction will occur with formaldehyde in an alkaline medium so that a hydroxybenzyl alcohol is formed according to the Lederer-Manasse reaction. This hydroxybenzyl alcohol reacts with sulfite and forms a hydroxybenzyl sulfonic acid. The following illustrates the above-mentioned reactions:



The above-noted investigators attempted to apply their concept to sulfite pulping of pine heartwood by pretreating it with a relatively concentrated solution of formaldehyde (20 percent concentration) in an alkaline (0.1 N NaOH) or aqueous solution at elevated temperature (80° C.) for 6 hours. Pulp made by this procedure showed greatly improved yield, but was still not satisfactory owing to low brightness (discoloration) as well as shiviness.

A process overcoming the deficiencies in the treatments just discussed is described in copending U.S. application Ser. No. 539,683 filed Apr. 4, 1966. This process is based on the discovery that, in contrast to previously described findings, considerable improvements not only in the pulping of pines, but also of other coniferous woods such as spruce, occur if the pretreatment of the pine chips is carried out both at a low temperature and at a low concentration of formaldehyde in alkali. Impregnation temperatures preferably below about 5° C. and formaldehyde concentrations between about 0.15 and 0.4 percent, corresponding to 0.75 percent to 2.0 percent (added) by weight based on wood at an alkali solution-to-wood ratio of 5:1 by weight, result in highly significant improvements. Such process is denominated the AFS-process, and is distinguished from the so-called ACSNa and AS-processes in the copending application. (AFS=Alkaline formaldehyde pretreatment followed by sulfite pulping; ACSNa=acid sulfite pulping with sodium base; and, AS=alkali pretreatment followed by sulfite pulping.)

The low formaldehyde concentration and the low impregnation temperature promote the reaction of pinosylvin and other polyphenolic compounds according to the Lederer-Manasse reaction and substantially slow or prevent the otherwise competing, but undesired lignin-formaldehyde condensation, which proceeds disadvantageously at an increased speed at a higher concentration of formaldehyde and at a higher temperature.

Experimental results on jack pine presented in the above-noted, copending application show that unbleached pulp yield, brightness, and viscosity are increased by the alkaline formaldehyde pretreatment, reaching maxima between 2 and 4 percent formaldehyde. All these properties decrease as temperature is increased above about 40°–50° C.

AFS-jack pine pulp in comparison with a conventional soda base sulfite pulp shows 9 points gain in brightness and a 5 percent actual gain in screened pulp yield. Corresponding gains for AFS-black spruce pulp are a 7-point gain in brightness and 6 percent actual increase in screened pulp yield. AFS-Douglas fir showed a 3 percent higher actual yield and 12.5-point gain in brightness in comparison with the corresponding AcSNa pulp. Other properties, such as high viscosity and high mannan content, reflect the unique characteristics of pulps from alkali-formaldehyde pretreated wood.

Paper strength tests of AFS pulps showed that they are equal to conventional sulfite pulps at a freeness of 300 CSF, but surpass them at a freeness of 100 CSF. Consequently, such pulps make very satisfactory paper pulps both for unbleached and bleached grades, but are particularly suitable for glassine-type pulps as a result of fast beating and good retention of strength in beating to low freeness.

It has now been found that the alkaline formaldehyde pretreatment gives similar or even greater advantages when used in connection with the bisulfite cooking process, so denominated because base and sulfur dioxide are present in the stoichiometrical proportions to give only the bisulfite, without excess of either constituent. The complete operation is here referred to as the AFB process.

AFB cooking conditions are obtained by treating NaOH-CH_2O-impregnated chips with an aqueous sulfurous acid solution which contains the amount of SO_2 required to produce sodium bisulfite instead of the free-SO_2 required to produce sodium bisulfite instead of the free-SO_2-containing sodium acid sulfite liquor. Instead of the aqueous solution, liquid SO_2 may be employed, the choice depending largely on local availability.

Bisulfite is formed stoichiometrically according to the following equation:

$$NaOH+SO_2+H_2O \longrightarrow NaHSO_3+H_2O \quad (1)$$

This reaction should lead to pH 4. However, in practice it has been found that the actual quantity of SO_2 should be about 2 to 8 percent less than the theoretically calculated one. This has been found desirable in order to prevent a substantial lowering in pH (resulting from wood acids produced during cooking) below the bisulfite range.

The general method of the present invention is as follows:

A blend, for instance, of balsam-spruce chips is treated with a sodium hydroxide solution containing a small quantity of formaldehyde. The liquor is drained after the required time of impregnation. The amount of NaOH taken up by the chips is determined by measuring both volumes and NaOH contents of the fresh liquor added and the drained liquor recovered. The amount of SO_2 required to form bisulfite is calculated less 6 percent based on equation (1) and a sulfurous acid solution containing the required quantity of SO_2 is injected into the digester. A cold pH preferably between 3 and 4 will be reached after a few hours of cooking. It should also be understood that the time-temperature cooking chart used is designed to allow for ample diffusion time of chemicals from the outside of the chips toward the center and vice versa before a substantial temperature rise occurs.

For a clearer understanding of the present invention, reference should be had to the following example:

example 1

[Wood: Balsam-spruce mill chips (10,500 g. oven-dry weight)]

Caustic impregnation

Liquor:	
NaOH, grams/litre	50
CH_2O, grams/litre	4
Volume added, liters	54
Temperature, ° C	25
Liquor to wood ratio	5.1:1
Pressure, p.s.i.	100
NaOH take-up, g.	1,167

Bisulfite cook

Liquor:	
Sulfurous acid, SO_2, percent	4.12
Volume added, liters	44.4
SO_2 content, grams	[1] 1835
pH	3.5
Liquor to wood ratio	4.2
Max. cooking temperature, ° C	155
Pressure, p.s.i.g	[2] 85

[1] 30 grams less than that required for complete formation of $NaHSO_3$.
[2] Constant from start to finish.

COOKING CHART

Time, hours	0	1	2	3	4	5	6	7	8	8½
Temp., ° C	25	40	50	90	125	155	155	155	155	155
Pressure, p.s.i.g	85	→								
Total SO_2 %	3.06	2.85	2.7	2.6	2.58	2.10	1.54	1.06	0.76	0.66
Combined SO_2 %	0.96	1.16	1.2	1.19	1.18	0.9	0.64	0.46	0.32	0.28
Cold pH	2.1	2.5	2.56	2.70	2.75	2.90	3.10	3.40	3.5	3.45

It should be understood that variations of the procedure of the example such as, for instance, caustic impregnation with lower concentrations of NaOH and CH_2O also produce satisfactory results. Furthermore, other caustic impregnation media including the strongly alkaline carbonates of such bases or a combination of carbonates with alkalies are within the scope of this invention, and indeed have certain advantages which will be discussed later.

Results produced in accordance with the AFB process of the present invention are shown in FIG. 4 (table 1*a*) and are compared with four conventional sodium bisulfite process (pH 4) controls reported in FIG. 5 (table 1*b*). For simplicity, such conventional process is designated therein as the BSNa process. The same spruce-balsam blend was used in all cases.

It should be noted that AFB high-yield pulps were obtained, with one exception, as screenable pulps without the need of mechanical refining. In contrast, the conventional bisulfite pulps required mechanical refining.

Advantages of AFB pulps over conventional bisulfite pulps are the following:

1. Screened pulp yields of about 60 percent without mechanical refining (this is due to better delignification and higher retention of hemicelluloses);
2. Pulps at yields above 60 percent and up to 75 percent can be obtained by mild refining in a single-pass operation;
3. Considerably higher unbleached brightness; and,
4. Good strength characteristics except somewhat lower tear and opacity.

The new AFB pulps are particularly valuable as a replacement for ordinary unbleached sulfite pulps, especially whenever higher brightness and high screened yield and good beatability are desired, as in newsprint or publication grade papers.

Replacement of NaOH with Na_2CO_3 or, preferably, a combination of Na_2CO_3 with NaOH in the impregnation stage of AFB cooking has been found to contribute further significant improvements in delignification, paper strength characteristics, and the brightness of AFB pulps. The following example illustrates such a cooking procedure and sets forth pulp data:

EXAMPLE 2

Conventional spruce-balsam mill chips were impregnated with a solution of 80 g. Na_2CO_3, 11 g. NaOH and 2.8 g. CH_2O per liter, at R.T. and 100 p.s.i. for 90 minutes at a liquor-to-wood ratio of 5:1. Three pressure cycles of 1 minute each were applied to improve liquor penetration. The liquor was then drained and an aqueous SO_2 solution was injected, containing the amount of SO_2 necessary to convert the base into sodium bisulfite according to the following reactions:

$$Na_2CO_3(NaOH)+SO_2(H_2O) \longrightarrow NaHSO_3+NaHCO_3$$

$$NaHCO_3+SO_2 \longrightarrow NaHSO_3+CO_2$$

Cooking was carried out according to the following chart for a total time of 6 hours, 5 minutes:

Time, hours	0	1	2	3	4	5	6
Temperature, °C.	RT	40	50	90	125	150	155
Pressure	90	90	85	110	90	90	90

The liquor-to-wood ratio was 4:1 using a full digester and maintaining 90 p.s.i. throughout the cook. The cooked chips were given a mild mechanical refining treatment. The above conditions produced the following pulp:

		Strength (PFI Mill) at 500 CSF:	
Pulp Yield	72.2%		
Brightness, % (Elr)	59	Mullen, % pts./lb.	140
Kappa number	95	Tensile strength, m.	12,500
Roe number	21.4	Tear Factor	70
		Fold (Schopper)	210
		Opacity, %	64

The following table shows pulp data for the two variations (i.e., NaOH+CH_2O and Na_2CO_3+NaOH+CH_2O) of the AFB process and comparative data for a conventional sodium bisulfite (BSNa) control cook. All data were extrapolated to 75 percent pulp yield for easier comparison:

Pulp Yield: 75%
AFB

PULP DATA	Na_2CO_3 +NaOH	NaOH	BSNa
Roe number	23.9	26.0	31.0

Table – Continued

Brightness, % (Elr)	60.0	58.5	56
PFI Strength at 500 CSF	143	124	140
Mullen, % pts./lb.			
Breaking Length, m.	12,500	10,300	11,800
Tear Factor	67	63	63
Mannan, %	15.7	13.7	11.8

FIGS. 1, 2 and 3 give the same comparison for Roe number, brightness and breaking length over a range of pulp yields.

The reaction between carbonate and also hydroxide with SO_2 proceeds primarily within the chip. The pH gradually decreases, CO_2 being generated until the formation of sodium bisulfite is completed. The initial pH during caustic impregnation is 12.5; however, decomposition of the carbonate starts below pH 8.5. Theoretically, for each mol (106 grams) of Na_2CO_3, 1 mol of CO_2 (44 grams or 22.4 liters at 0° C., 760 mm.) is formed. The solubility of CO_2 in water at a pressure of 80 p.s.i. and 30° C. is 0.4 gram CO_2/100 ml. H_2O. This will lower pH to 3.5. Therefore, this system containing excess CO_2 and carbonic acid is in a position to exert effectively within the chip a buffering action and, perhaps, also other not yet completely understood reactions during the initial stages of the bisulfite cook. It is suggested that the above-indicated effects are a contributing or even major factor in the striking improvement in pulp characteristics.

In the AFB process, as in the AFS process of copending U.S. application Ser. No. 539,683, alkaline impregnation at a hydrostatic pressure of 100 p.s.i.g. and at temperatures below 50° C. requires 90 minutes for uniform penetration of chips. If impregnation temperatures above 50° C. are applied, a significant lowering in both brightness and delignification rate occurs. Furthermore, it has been found that the conversion from alkaline to acid (bi) sulfite condition within the chips (which is controlled by a relatively slow diffusion) must be completed (requiring 90 minutes at 50° C. and 100 p.s.i.g.) before the chips can be subjected to higher cooking temperatures. Such measures are necessary to prevent the inactivation of lignin in an alkaline medium with its detrimental effects on the subsequent bisulfite cooking stage. The necessity for the above conditions has heretofore limited the AFS and AFB processes to slow batch cooking.

However, it has been discovered that the above limitations imposed by times and temperatures can be resolved by conducting both the caustic and the acid stages at pressures substantially above the 100 p.s.i.g. mentioned previously. Pressures in the neighborhood of 200 p.s.i.g. have been found adequate. Improvement levels off above this point although higher pressures may be used if desired. This modification shortens the Na_2CO_3+NaOH+CH_2O impregnation stage to a fraction of the previously required time, a few minutes only, and it also permits a rapid and complete conversion of the chemicals within the chip from an alkaline to an acid condition. Be it noted, however that the temperature employed in the impregnation should be kept as low as possible. With the short impregnation time (about 2 minutes) made possibly by use of 200 p.s.i.g. pressure, the upper limit should be about 100° C.

It has also been discovered that, as a result of the short exposure time to an alkaline environment, the otherwise detrimental effects of even moderately increased temperatures were no longer harmful. As a result of this, the previously imposed temperature restrictions and time requirements can be so modified as to make this process suitable for continuous pulping.

The following is a description of the principal features of a quick AFB process suitable for continuous operation:

Mill chips such as jack pine, spruce, balsam or blends are pretreated with an alkaline solution containing a mixture of sodium hydroxide, sodium carbonate, and formaldehyde, total Na_2O content 55 grams per liter, the proportion of carbonate being such that the CO_2 liberated during the subsequent acidification step will assist in holding the pressure at the level of the impregnation step, i.e. about 200 p.s.i.g. or above, while avoiding an excess of CO_2 which would have to be gotten rid of.

The composition of the caustic impregnation liquor must be adjusted in such a way that the combined strength of Na_2CO_3 and NaOH is sufficient to result in a minimum takeup of about 10 percent Na_2O on wood. The concentration of NaOH in the Na_2CO_3-containing liquor must be adequate to obtain a minimum pH of 12.6.

For practical application 80 to 100 grams Na_2CO_3 per liter and 11 to 5 grams NaOH per liter will satisfy the above requirement and also insure the desired pressures from the beginning of the cook. Lower amounts of Na_2CO_3 and correspondingly higher levels of NaOH can be used as long as the desired level of Na_2O on wood and the required pressure buildup are obtained.

If the carbonate content is reduced below a level necessary to liberate sufficient $CO_2$to maintain the pressure required for quick conversion to sulfite after the impregnation stage, other means of pressure generation must be provided. Continuous pulping with two sequential stages prevents the use of a full digester which would be necessary for the use of a booster pump to maintain pressure. However, adequate pressure can easily and cheaply be maintained by, for instance, an oil-burning inert gas generator-compressor combination as commonly used for inert gas padding. But it should be kept in mind that, aside from pressurizing, carbonate has a beneficial effect on pulp properties, as described previously.

The level of formaldehyde in the impregnation liquor chosen will depend on the wood species used. The upper limit of formaldehyde is 2 percent by weight, based on the wood (or 0.4 percent by weight of the liquor, based on a liquor-to-wood ratio of 5 to 1). Woods containing objectionable resins such as jack pine, will require between 1 and 2 grams of CH_2 (100 percent) per liter. On the other hand, less refractory woods such as balsam and spruce or blends can be adequately treated with liquors containing 0.25 to 0.5 grams CH_2O per liter. In making some pulp grades from these more readily pulped woods, the addition of even this small amount may not be economically justified—this will have to be decided by the requirements of the particular pulp grade and the current price of formaldehyde.

The impregnation liquor is applied at a liquor-to-wood ratio of 5 to 1 by weight and at a temperature between 20° C. and 50° C. and a pH of 12.8. The wood chips in the liquor are subjected to a hydrostatic pressure between 200 and 300 p.s.i.g. for 2 to 15 minutes. The impregnation liquor is then drained and made up to strength with Na_2CO_3 and NaOH (and CH_2O) for reuse in the next cook. After draining of the alkaline solution, water and liquid sulfur dioxide or an aqueous solution of sulfur dioxide is injected, so that a liquor-to-wood ratio of 4.5 to 1 is obtained. The temperature is then increased within 1 to 2 minutes to between 50° C. and a maximum of 100° C. The required quantity of sulfur dioxide is calculated to convert the alkali taken up by the wood into sodium bisulfite. Liberation of carbon dioxide from the ensuing reaction between Na_2CO_3 and SO_2 in the digester is regulated by pressure relief in such a manner as to maintain a constant pressure of at least 200 p.s.i.g. throughout the cook. As mentioned above, the required pressure may be obtained in whole or in part from a compressor-inert gas generator combination.

The following cooking chart is used:

Time Minutes	0	3	63	83
Temp., °C.	20–50	100	100	155 (max)
Pressure, p.s.i.g.	200	200	200	200 (max)

Total cooking times vary between 2 and 3 hours depending on the desired Roe number or pulp yield.

It should also be mentioned that the process of the present invention can be carried out as a full or partial vapor phase (trickle phase) process with all its inherent advantages owing to savings in steam and a further reduction in cooking time.

In this case, only liquid SO_2 and steam are admitted into the digester.

The method of the present invention is particularly suitable for high-yield semichemical pulping of softwoods, because the

resulting pulps have excellent fiberability, good uniformity and brightness, and high strength at pulp yields even above 70 percent. Such characteristics make this type of pulp a highly desirable component of groundwood furnishes for newsprint or for board making.

The outstanding fiberability characteristics of this pulp make it possible to obtain, without mechanical refining, high-yield fully chemical pulps in a yield range between 61 and 65 percent.

The following examples are given:

EXAMPLE 3: (High-yield, semichemical pulp)

Wood: White spruce (40 percent); balsam (60 percent); 12.0 kg.
Impregnation Liquor:
Na_2CO_2, anhydro.: 80 g./1.
NaOH: 11 g./1.
CH_2O: 0.25 g./1.
Impregnation Time, Min: 2
Impregnation Pressure, p.s.i.g.: 200
Impregnation Temperature: 40° C.
L:W (liquor:wood ratio) 5
pH 12.8
Chemical take up:
Na_2CO_2: 1,180 grams
NaOH: 465 grams
CH_2O: 15 grams
The impregnation liquor was drained and an aqueous SO_2 solution containing 2,145 grams of SO_2 was injected. The following heating schedule was applied:
Time to 100° C: 3 minutes
Time at 100° C.: 60 minutes
Time to 155° C.: 20 minutes
Time at 155° C.: 95 minutes
Total Time: 178 minutes
pH after 1 hour: 2.3
pH-maximum: 3
The pulp was refined in a disc refiner in a single pass at a plate clearance of 0.020 inch.
The following pulp characteristics were obtained:
Pulp Yield, percent: 75
Brightness, percent, by Zeiss "Elrepho" Photometer: 56
Roe number: 27.8
Fiberability,* percent: 90

*Fiberability is based on a test comprising defibration for 45 seconds at 3 percent consistency, L-speed setting in a Waring Blendor, model CB–5, followed by screening on a Valley Iron 12 cut laboratory screen.

Strength Properties at 500 CSF:
Tear Factor: 51
Mullen, percent pts/lbs: 110
Tensile Strength, m.: 9,600

A pulp of good brightness and exceptionally high fiberability was obtained. It should be mentioned that high fiberability and greater ease in mechanical refining are closely related. The strength properties of this pulp are comparable to conventional batch-type AFB pulps, with the exception of mullen which is somewhat lower.

EXAMPLE 4: (High-yield semichemical pulp, lower proportion of NaOH in impregnation)

Wood: White Spruce (40 percent); Balsam(60 percent); 3,500 grams
Impregnation Liquor:
Na_2CDO_3, anhydr., g./l.: 95
NaOH, g./l.: 5
Liquor-to-wood Ratio: 5
Chemical takeup:
Na_2CO_3, grams: 588
NaOH, grams: 52
The impregnation liquor was drained and an SO_2 solution containing 619 g. SO_2 was injected. The following heating schedule was applied:
Time to 100° C., min: 2
Time at 100° C., min: 60
Time to 155° C., min 10
Time at 155° C., min: 55
Total cooking time, min.: 127
pH (cold) after 1 hr: 2.5
pH (cold) maximum: 2.9

Pulp Yield, % 73.0
Brightness, (Elr), % 59.3
Fiberability, % 72.3
Roe Number 25.3

Strength at 500 CSF:
Tear Factor: 52
Mullen, % pts./lb.: 147
Tensile strength, m.: 11,600

The above cook was carried out with a lower proportion of NaOH. It should be noted that the decrease in NaOH content was accompanied by a decrease in fiberability. However, the cooked chips could still be refined in a single pass operation.

EXAMPLE 5: (High-yield, fully chemical pulp)

Wood: White Spruce (40 percent) Balsam (60 percent); 12.0 kg.
Impregnation liquor and impregnation conditions same as in example 1, with the omission of formaldehyde.
Chemical takeup:
Na_2CO_3: 1,760 grams
NaOH: 453 grams
The impregnation liquor was drained and an aqueous SO_2 solution containing 2,750 grams SO_2 was injected.
The following heating schedule was applied:
Time to 100° C., min: 3
Time at 100° C., min: 60
Time to 155° C., min: 20
Time at 155° C., min: 107
Total cooking time, min: 190
pH (cold) after 1 hour: 2.7
pH (cold) maximum: 2.9
This pulp was in slush form after blowing the digester; no mechanical refining was required.
Pulp Yield, percent: 62
Brightness, percent Elr: 55
Fiberability, percent: 99
Roe Number: 13
Strength properties at 500 CSF
Tear Factor: 47
Mullen, percent pts./lb. 137
Tensile Strength, m. 12,000
It should be noted that screenable pulp was obtained at a yield of 62 percent. Only a "touch up" operation in refining was needed to break up a small amount of screenings. In contrast, the screenable limit of conventional bisulfite pulp is in the neighborhood of 54 percent. A comparison of examples 3 and 5 shows the relatively small effect of formaldehyde in the case of spruce-balsam, the principle effect being a small gain in brightness.

EXAMPLE 6: (High-yield, semichemical pulp)

Wood: A blend of:
jack pine, percent: 15
balsam, percent: 51
white spruce, percent: 34
Impregnation liquor:
Na_2CO_3, anhydr., g.: 80
NaOH, g.: 11
CH_2O, g./l.: 0.5—1.0
Impregnation and cooking conditions correspond to those described for example 1, except for the higher level of formaldehyde.
Pulp Yield, percent: 78
Brightness, percent Elr: 56
Roe Number: 28
Fiberability, percent: 77
Strength properties at 500 CSF:
Tear Factor: 58
Mullen, percent pts./lb.: 110
Tensile strength, m.: 9,500
The above example shows that the use of formaldehyde per-

mitted the addition of jack pine to a balsam-spruce blend without detriment to pulp brightness and other properties. This is in contrast to an otherwise well-known lowering pulping characteristics resulting from an addition of jack pine.

The following table of comparative figures taken from the preceding examples shows the reduction in time for process steps effected by the increase in pressure. Figures illustrative of conventional bisulfite pulping are added for comparison.

Cooking Stages	AFB (Batch type)	AFB (Continuous type)	BSNa Conventional
Alkali Impregnation Stage			
Time, minutes	90	2	none
Pressure, max., p.s.i.g.	100	200	—
Bisulfite Cooking Stage			
Time to max. temp., hrs.	6:00	1:23	6:00
Time at max. temp., hrs.	0:30	1:00	0:40
Pressure, max., p.s.i.g.	100	200	85
Temperature, max., °C.	155	155	160
Total Cooking time, hrs.	8:00	2.25	6:40
Pulp Yield, %	73.0	73.4	73.2

The large reduction in cooking times makes it possible to obtain the previously described advantages of the AFB batch cooking process in a continuous pulping operation.

For more positive pH control in continuous cooking, the SO_2 injected into the digester may be replaced by a solution of bisulfite (containing excess SO_2). Part of this is made to flow countercurrently to the alkali-treated chips, displacing alkali and leaving the chips impregnated with bisulfite. The alkalized bisulfite solution is withdrawn from the digester and regenerated with SO_2 in an absorption tower for subsequent reuse. A process embodying these features will form the subject of a further application.

What is claimed is:

1. A process for making pulps of increased pulp yield, high unbleached brightness and high fibrability from coniferous wood, comprising impregnating the wood with an alkaline solution containing not more than about 2 percent by weight of formaldehyde at a pH of about 12.5 at a temperature not exceeding about 100° C. and a pressure between about 100 and about 300 p.s.i.g., draining the solution from the wood, adding liquid or aqueous SO_2 so as to obtain a bisulfite cooking condition, and cooking to obtain maximum pH between about 2.9 and about 4.

2. The process of claim 1 wherein the alkaline solution is a mixture of hydroxide and carbonate.

3. A process as in claim 1 wherein the maximum pH is 2.9.

4. A process as in claim 1 wherein the maximum pH is 3 .

5. The process of claim 1 wherein the alkaline impregnation is carried out for about 90 minutes at a temperature not exceeding about 50° C. and a pressure of about 100 p.s.i.g. is employed.

6. A process of claim 1 wherein a short alkaline impregnation of about 2 minutes is carried out at about 200 p.s.i.g. pressure at a temperature not exceeding about 100° C.

7. The process of claim 1 wherein SO_2 is injected in liquid or aqueous form after draining of the impregnation liquor and the cook is carried out in a vapor or trickle phase.

8. A process as in claim 1 wherein the impregnation pH is not lower than 12.6

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