Nov. 18, 1969 J. H. KALISCH 3,479,249

PRETREATMENT OF WOOD PULPS WITH AN ALKALINE SOLUTION OF FORMALDEHYDE

Filed April 4, 1966 4 Sheets-Sheet 1

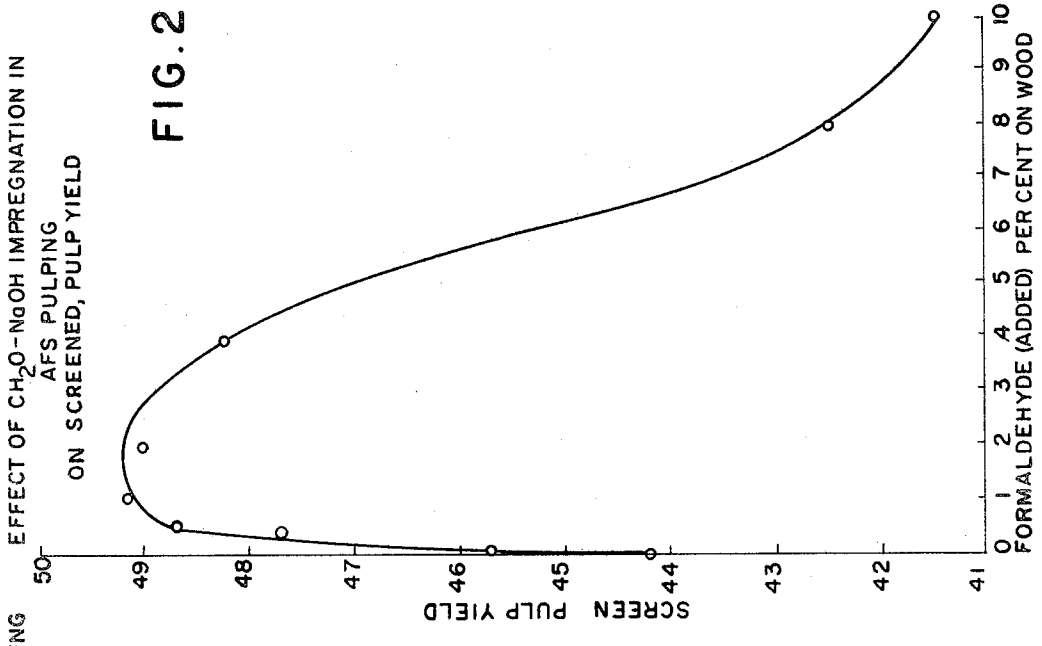


FIG. 2

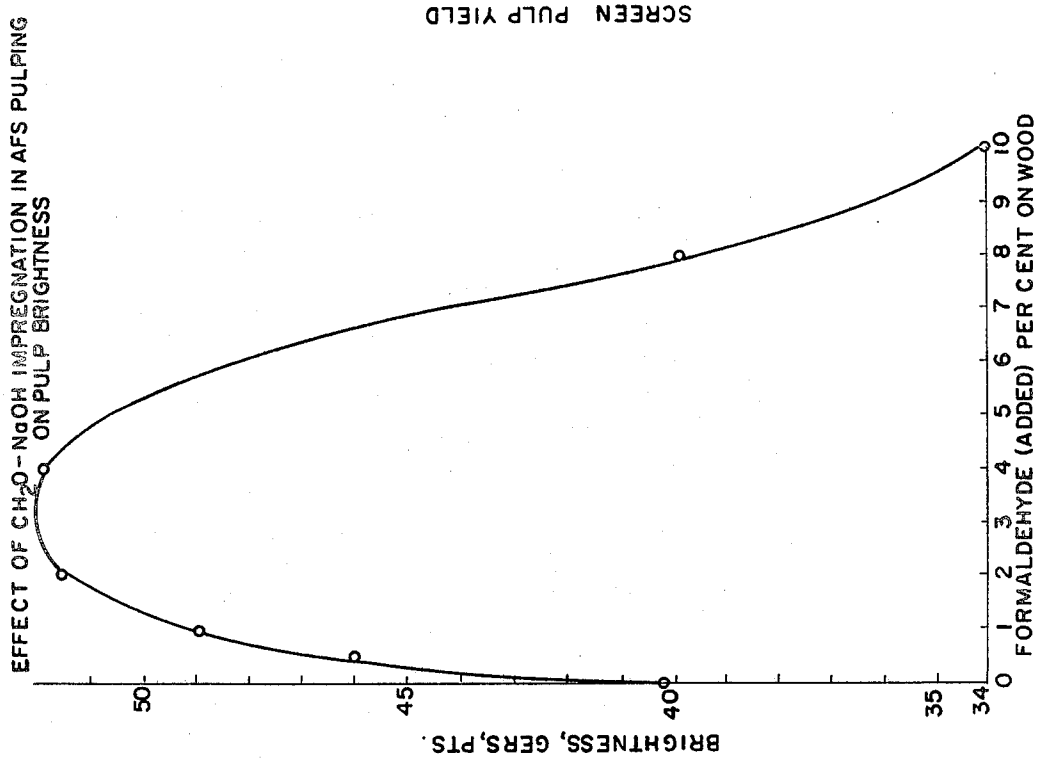


FIG. 1

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FIG. 6

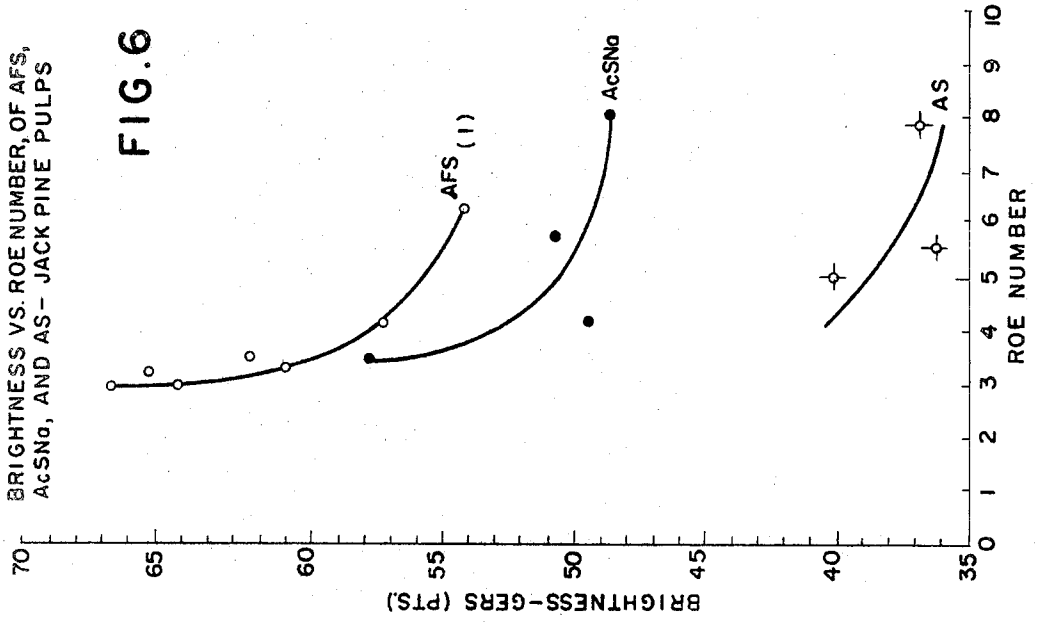
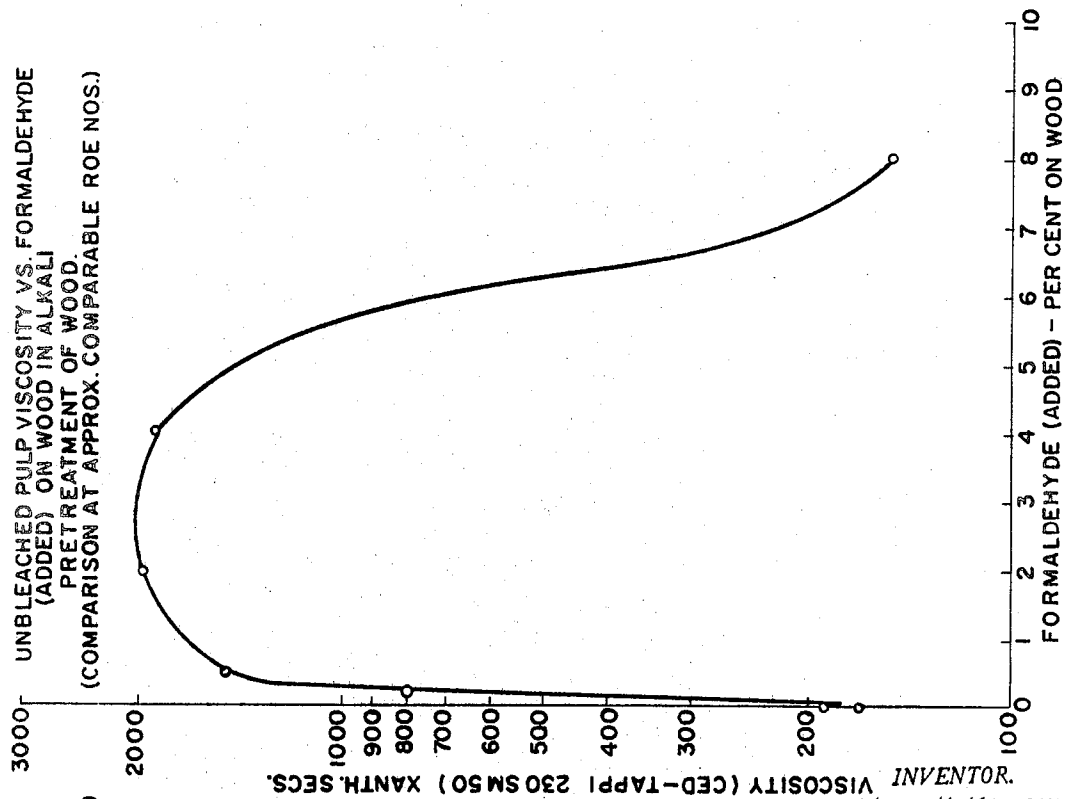


FIG. 3



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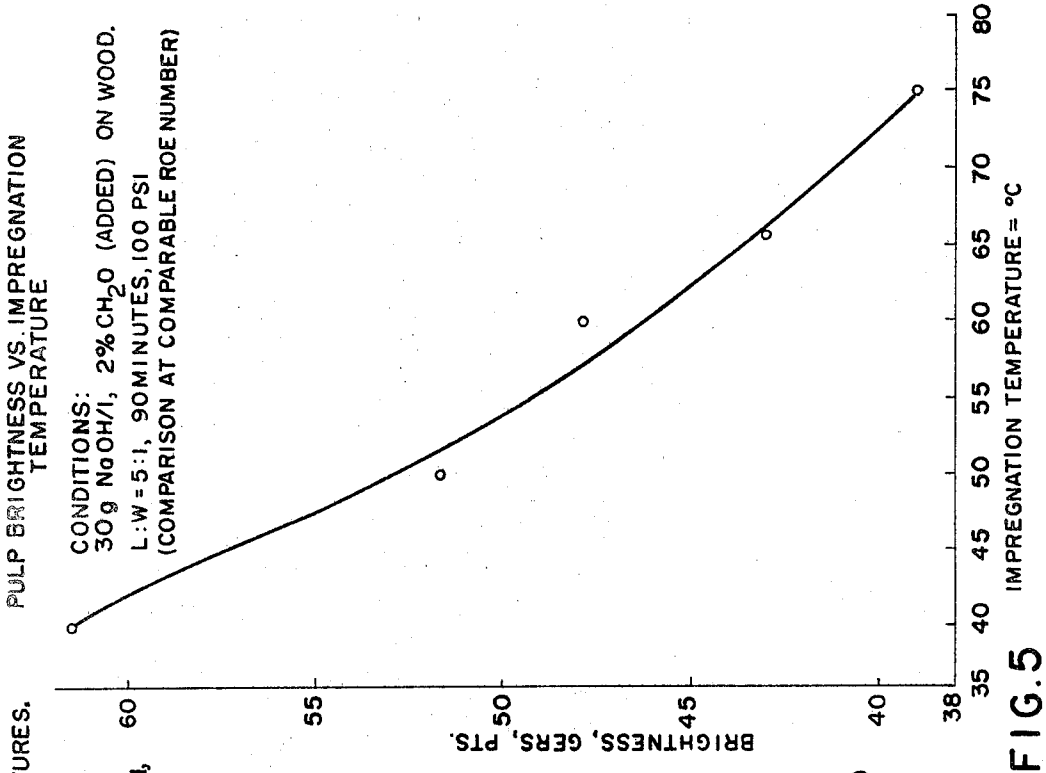


FIG. 5

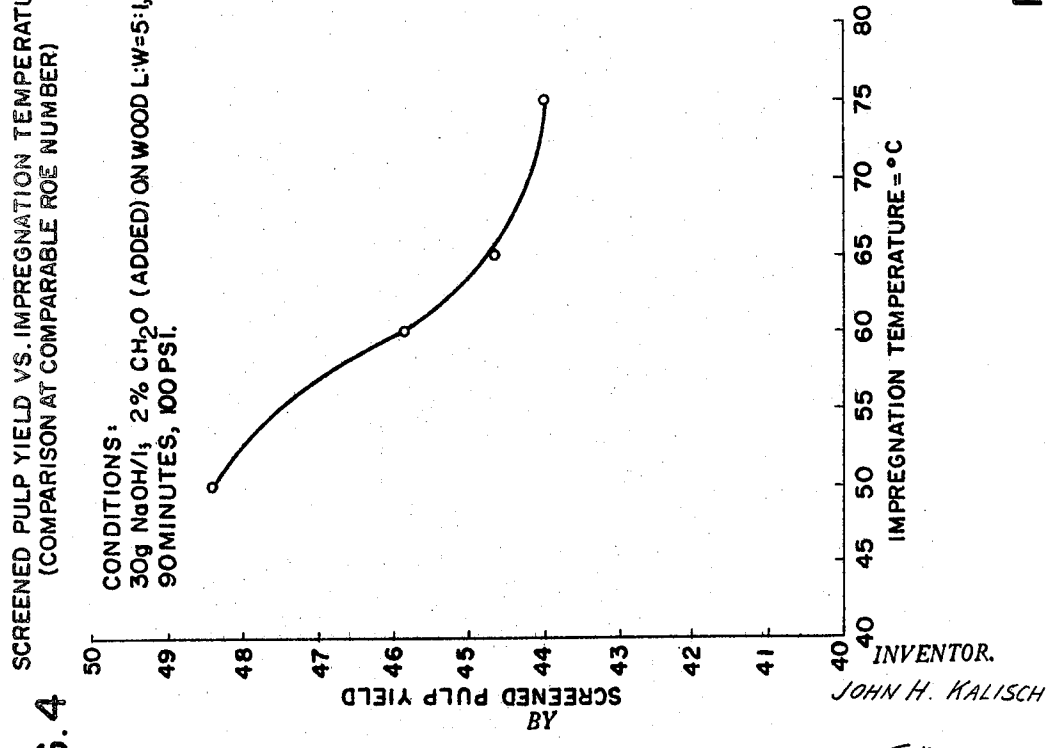


FIG. 4

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FIG. 7

WOOD SPECIES	JACK PINE (1)			BLACK SPRUCE			WHITE PINE		DOUGLAS FIR	
PULP TYPE	AFS (2)	AS (3)	AcSNa(4)	AFS	AS	AcSNa	AFS	AcSNa	AFS	AcSNa
SCREENED PULP YIELD, %	47.0	44.2	42.0	49.8	48.2	43.5	45.6	42.0	48.9	46.0
SCREENINGS, % ON WOOD	0.6	0.8	1.0	0.4	0.1	1.0	1.6	3.1	0.3	0.5
ROE NUMBER	3.0	5.0	3.4	1.5	1.1	1.6	4.8	4.9	1.0	2.3
VISCOSITY (TAPPI, 230 SM 50) CPS.	31.6	17.2	19.0	34.5	29.8	26.0	28.3	21.2	29.4	26.4
BRIGHTNESS, GERS, PTS.	66.8	40.2	57.8	69.5	56.5	62.3	59.4	56.9	59.5	47.0
ALPHA CELLULOSE %	84.4	86.9	87.5	84.7	85.0	88.7	81.1	85.7	88.3	90.3
PENTOSAN %	3.6	2.8	3.0	3.8	3.4	3.8	2.4	2.8	2.7	2.1
MANNAN %	11.3	9.7	4.9	11.7	9.7	6.4	10.2	6.0	9.6	7.1
XYLAN %	3.3	2.8	2.6	4.1	—	4.5	2.3	3.2	1.8	1.8
RESIN %	2.1	1.5	2.5	0.6	0.7	0.7	2.5	2.9	0.4	0.6
LIGNIN %	0.9	3.6	1.4	0.7	0.7	0.7	1.7	2.1	0.1	1.4

(1) AVERAGE AGE: 66 YEARS
(2) AFS: SULFITE COOKING OF ALKALI-FORMALDEHYDE PRETREATED WOOD
(3) AS: SULFITE COOKING OF WOOD PRETREATED WITH ALKALI ONLY
(4) AcSNa: CONVENTIONAL SODA BASE SULFITE COOK

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PRETREATMENT OF WOOD PULPS WITH AN ALKALINE SOLUTION OF FORMALDEHYDE

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Int. Cl. D21c 3/26
U.S. Cl. 162—18 4 Claims

ABSTRACT OF THE DISCLOSURE

A process for making pulps of high unbleached brightness and increased pulp yield from coniferous wood comprising pretreating the wood with an alkaline solution of formaldehyde at a temperature of between 20° C. and 50° for 90 to 120 minutes, the alkaline solution containing from 2.5% to 3.5% sodium hydroxide and from 0.15% to about 0.4% formaldehyde, and the proportion of solution to wood being 5 to 1 by weight. A conventional sulfite cook then results in a pulp of improved yield and brightness.

This invention 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 sulphite 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 sulphite process. The sulphite process is discussed at lengtfi 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 sulphite process. The use of soluble bases such as sodium, magnesium, and ammonium has led to substantial improvements over calcium base cooking. Pine chips from young trees can be successfully cooked by the conventional calcium base sulphite 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.

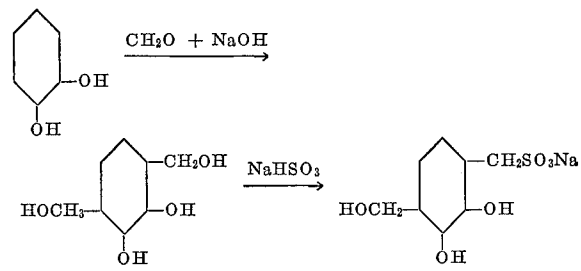
It has been shown that the heartwood portion of pines is responsible for their more difficult pulping characteristics; sapwood, on the other hand, pulps satisfactorily with any base by the sulphite process. Consequently, the relatively high proportion of heartwood in slow growing trees of normal age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

Hagglund (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 sulphite cooking. Such compounds were identified by Erdtmann as resorcinol-like polyphenols such as pinosylvin, pinosylvin methyl ether, and flavanones which amount to about 20% of the total resin of pine or to approximately 1% 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 sulphonation and final solubilization of the lignin.

Blocking of the reactive position of the polyphenol prior to the start of the sulphite cook is needed to prevent condensation with lignin. Experiments by Adler 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 sulphite and forms a hydroxybenzyl sulphonic acid. The following illustrates the above-mentioned reactions:



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

The object of the present invention is to overcome the deficiencies in the treatments just discussed and, thus, to obtain an improvement in the sulfite process permitting:

(1) satisfactory pulping of such refractory wood as pines;

(2) improved yields, combined with improved delignification resulting in high brightness; and,

(3) lessened degradation of the cellulosic and hemicellulosic components shown by a higher level of viscosity and improved physical properties, notably at low freeness values.

In contrast to previously described findings, it has now been found that considerable improvements in pulping not only of pines, but also 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 temperature preferably below 50° C. and formaldehyde concentration between 0.15 and 0.4 percent, corresponding to 0.75% to 2.0% (added) by weight based on wood at an alkali solution-to-wood ratio of 5:1 by weight, result in highly significant improvements.

The low formaldehyde concentration and the low impregnation temperature in the process of the present invention promote the reaction of pinosylvin and other polyphenolic compounds according to the Lederer-Manasses 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.

For a better understanding of the consequences of the process of the present invention, reference should be had to the attached drawings in which

FIGURE 1 illustrates the effect of CH_2O in pretreatment of jack pine on pulp brightness (it can be seen, for instance, that an addition og 2% CH_2O on wood increases brightness by 12 points GERS);

FIGURE 2 shows the influence of the addition of formaldehyde on screened pulp yield of jack pine (for instance, 2% CH_2O on wood increases screened pulp yield by five percent in comparison with a pulp which was made from wood treated with alkali only);

FIGURE 3 indicates the effect of CH_2O in pretreatment of jack pine on pulp viscosity (very significant increases in viscosity are shown with increasing quantities of formaldehyde, though an optimum is reached at about % CH_2O on wood added, and even very low quantities of CH_2O such as 0.2% CH_2O (added) on wood result in a very substantial rise in viscosity);

FIGURES 4 and 5 show the effect of impregnation temperature on screened pulp yield and brightness, respectively, in pretreatment of jack pine with NaOH plus CH_2O (it is shown that a lowering in impregnation temperature produces substantial increases in yield and in brightness); and,

FIGURE 6 shows Roe number—brightness correlation for jack pine pulps made by the AFS, AcSNa, and AS—processes. (AFS=Alkaline formaldehyde pretreatment followed by sulfite pulping in accordance with the present invention; AcSNa=acid sulfite pulping with sodium base; and, AS=alkali pretreatment followed by sulfite pulping).

FIGURE 7 is Table I which shows a comparison of pulps made by the process of the present invention and other processes.

A comparison of AFS and AS pulps shows the large gain in brightness as a result of the addition of formaldehyde to the caustic pretreatment liquor. Furthemore, in the case of AcSNa pulps, no further increase in brightness is obtainable; additional cooking results in a drastic lowering of the degree of polymerization (DP) without significant change in Roe number. In contrast, the AFS pulp showed a much higher brightness at even lower Roe number without any critical lowering in DP-values. It should be realized too that the effect of alkaline pretreatment alone (i.e., without the use of formaldehyde in the caustic pretreatment), as proposed by Rydholm et al. (Svensk Papperst. 64,386 (1961)), Croon (Svensk Papperst. 66 (No. 1) 1 (1963)), and others, is not satisfactory in the case of pine.

The following example further illustrates the process of the present invention:

Mill chips of pine such as jack pine, white pine, or black spruce and others, are pretreated with a solution of 2.5% to 3.5% sodium hydroxide containing between 0.25% to 0.4% formaldehyde at a solution-to-wood ratio of 5:1 by weight and a temperature between 20° C. and 50° C. for from about 90 to 120 minutes. The liquor is forced into the chips by four successive pressure purges in the completely filled digester. This is done either by applying a pressure of 100 p.s.i. hydrostatically or with an inert gas holding this pressure for 1 minute and relieving rapidly. After completion of the last pressure purge, a constant pressure of 100 p.s.i. is applied for 90 to 120 minutes. The impregnation liquor is drained into a make-up tank after the specified holding time and made up to strength with sodium hydroxide and formaldehyde for re-use preliminary to the next cook.

After complete draining of the alkaline formaldehyde from the chips, an aqueous solution of sulphurous acid

containing 6% to 7% SO_2 is pumped into the digester at a liquor-to-wood ratio of 5:1, so as to fill the digester to its maximum capacity. Digester pressure is maintained from the beginning to the end of the cook at 85 p.s.i.

The following cooking chart is used:

Time, hrs	0	½	1	2	3	4	5	[1] 6
Temp., ° C	40	50	77	100	118	128	136	[1] 142

[1] Max.

Cooking time varies according to the desired Roe No. level between 7½ and 9 hours.

Sodium hydroxide consumption is between 6.5% and 7.5% by weight based on wood and formaldehyde consumption is between 0.5 and 1% by weight based on wood.

Table I (FIGURE 7) shows a comparison of pulps made from jack pine (average age: 66 years) by the AFS (i.e., sulfite cooking of alkali-formaldehyde pretreated wood) process of the present invention, by the AS (i.e., sulfite cooking of wood pretreated with alkali only (30 g. NaOH/L., 50° C.)) process, and the AcSNa (i.e., the conventional soda base sulfite) process. In addition, data bearing on the pulping of black spruce (AFS, AS, AcSNa) and of white pine and Douglas fir (AFS, AcSNa) are set forth in Table I.

The alkali-formaldehyde impregnation of these woods was carried out at 40° C. instead of 50° C. in comparison with earlier experiments and it will be seen that this lowering of temperature contributed to additional gains in brightness for the pulps.

The data of Table I show that the limited use of formaldehyde under certain conditions is solely responsible for the exceptionally high brightness of the AFS-pulps. Furthermore, the limited addition of formaldehyde contributed to higher yield and higher viscosity of the AFS-pulp as can be seen in comparison with an AS-pulp. AFS-jack pine pulp in comparison with a conventional soda base sulfite pulp shows 9 points gain in brightness and a 5% actual gain in screened pulp yield. Corresponding gains for AFS-black spruce pulp are a 7 point gain in brightness and 6% actual increase in screened pulp yield. AFS-Douglas fir showed a 3% 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 sulphite 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 also been found that the alkaline formaldehyde pretreatment disclosed herein gives simliar or greater advantages when used in connection with the bisulphite cooking process in which the base and sulfur dioxide employed to pulp the wood chips are present in stoichiometrical proportions, without an excess of either reactant, so as to yield only the bisulphite. The discussion of such improved process, called the AFB process, is being covered in a second patent application.

What is claimed is:

1. A process for making pulps of high unbleached brightness and increased pulp yield from coniferous wood comprising,

(1) Pretreating the wood with an alkaline solution of formaldehyde at a temperature of between 20° C. and 50° C. for 90 to 120 minutes, said solution containing from 2.5% to 3.5% sodium hydroxide and

from 0.15 to about 0.4% formaldehyde, the proportion of said solution to said wood being 5 to 1 by weight,

(2) Applying elevated pressure to the said wood with said solution such that said wood is impregnated with said solution,

(3) Draining the alkaline solution from the wood,

(4) Cooking the wood in accordance with the sulfite process.

2. The process of claim **1** wherein the pressure is about 100 p.s.i.

3. The process of claim **1** wherein the wood is chosen from the group consisting of jack pine, white pine, black spruce and Douglas fir.

4. The process of claim **3** wherein the pressure is about 100 p.s.i.

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S. LEON BASHORE, Primary Examiner

R. H. TUSHIN, Assistant Examiner

U.S. Cl. X.R.

162—72