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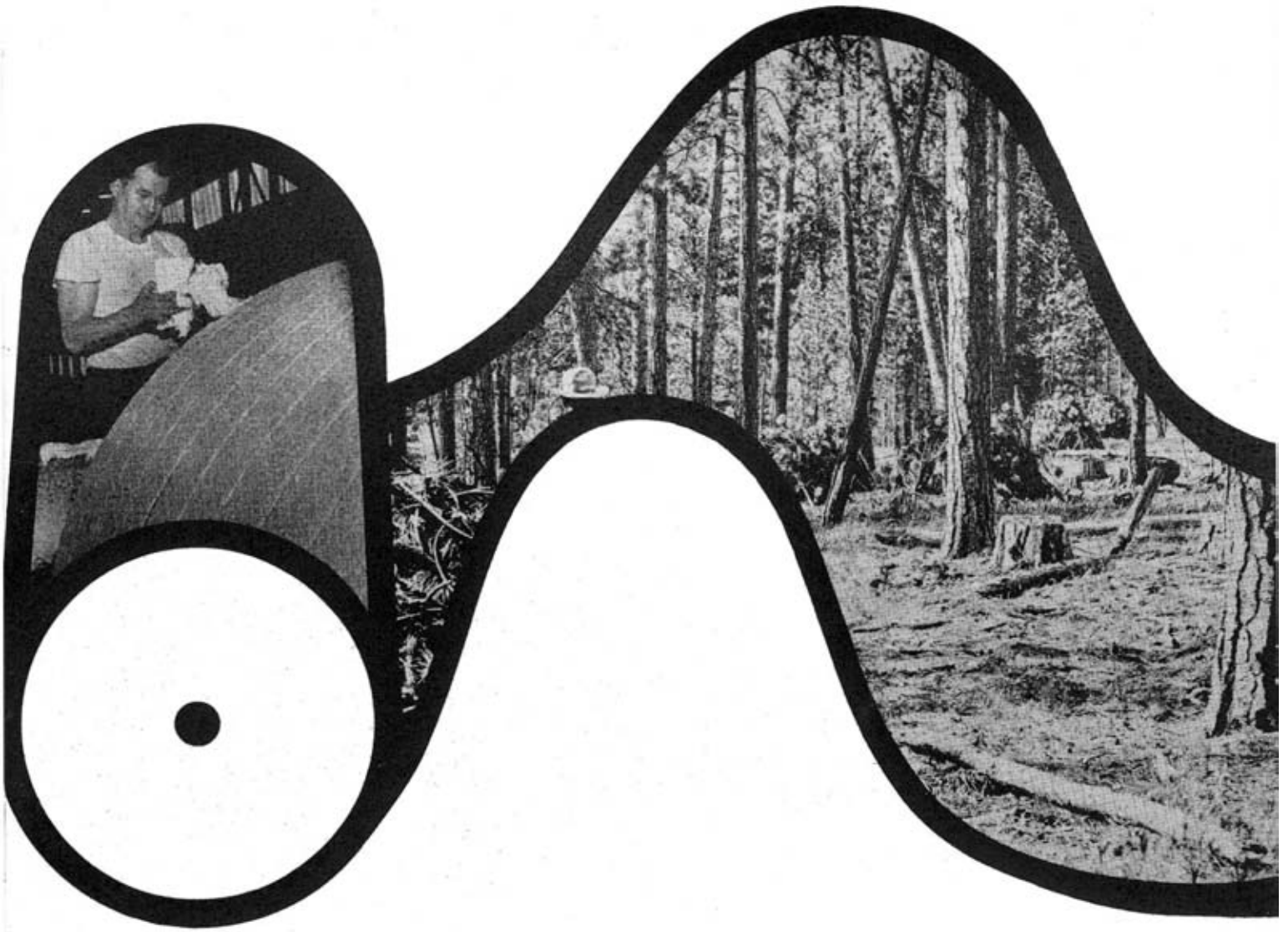

MAGNESIUM BISULFITE PULPING AND PAPERMAKING WITH SOUTHERN PINE

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Summary

Southern pine, which does not respond to the conventional sulfite process because of the phenolic extractives of its heartwood, was readily pulped with magnesium bisulfite. The pitch problem common to pine pulps cooked by nonalkaline processes was avoided by storing the logs for some months before cooking. Although such storage typically results in blue stain of the wood. the unbleached sulfite pulp was much brighter than kraft pulp and was further improved by treatment with brightening agents. The pulp was fully bleached using only chlorine, caustic extraction, and hypochlorite in three stages compared to five-stage bleaching, which included two chlorine dioxide stages, used for a kraft pulp made from the same lot ofwood.

In addition to lower cost for bleaching the pulp, the spent liquors of the magnesium bisulfite pulp can be burned to recover heat and chemicals at a lower cost than for recovery in the kraft process, particularly in small- or medium-size mills.

The use of unbleached and bleached pulps as the top ply of linerboard and in various printing and writing papers, toweling, and tissue papers was successfully demonstrated.

The process is attractive wherever the quality of the pulp is adequate because, compared with a kraft mill, a much smaller yet economically sound sulfite mill can be built.

Magnesium Bisulfite Pulping and Papermaking with Southern Pine[1]

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Introduction

Pulping wood by a sulfite process rather than the kraft process has advantages in producing a pulp that can be used in some light-colored products without bleaching and can be readily bleached for others. If pine heartwood is used, however, conventional sulfite pulping liquors of calcium bisulfite plus a great excess of sulfur dioxide frequently decompose before pulping is complete. A dark pulp results that contains many screening rejects, requires a large quantity of bleach, and has low strength, The heartwood contains phenolic extractives that condense with the lignin when wood is digested under acidic conditions. This blocks the sulfonation reaction essential to dissolve the lignin and release the wood fibers (5).[3] Under these conditions, cooking continues until sufficient byproducts accumulate to precipitate the lime as sulfate and decompose the liquor.

Pine heartwood, however, can be pulped successfully with bisulfites in the absence of excess sulfur dioxide. The lower acidity slows condensation sufficiently to allow adequate sulfonation. Because the calcium salt is insoluble, a soluble bisulfite such as sodium, ammonium, or magnesium must be used. Magnesium bisulfite liquor was successfully applied on a laboratory scale in 1941 to Douglas-fir (4), which, like pine, is resistant to conventional sulfite pulping because of phenolics in the wood. Magnesia base took on economic potential some years later when a recovery system for the magnesia and sulfur in acid sulfite spent. liquors was announced. In extending the recovery system to include magnesium bisulfite liquors it was shown that jack pine could be pulped readily (8). Recently, introduction of fluid bed combustion reduced the minimum investment required and made it practicable for use in smaller mills (1).

Magnesium bisulfite pulping has never been applied to the southern pines, which have been regarded as especially resistant to pulping because of their extremely high content of resins. A southeastern mill, however, pulped these species for several years with sodium bisulfite followed by an alkaline extraction to remove the excess pitch (7).

Compared with a kraft mill, a sulfite mill has

[1] This work was done in cooperation with Mississippi state University, State College, Miss.
[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
[3] Numbers in parentheses refer to Literature Cited at the end of this report.

the advantage of requiring a lower plant investment. Under favorable conditions a magnesium bisulfite mill of 150-ton capacity, or even less, can be profitable when equipped with fluid bed combustion for the recovery of cooking chemical; a kraft mill must be about twice this size to justify the high cost of the kraft recovery system The sulfite mill also has the advantage of smaller operating costs for bleaching.

The South, dominated by the kraft industry, offers potential local markets for the unique properties of sulfite fibers. Southern conifers are less costly than the northern. These factors, added to the economic advantages of the sulfite mill, led to this investigation of pulping, bleaching, and papermaking with southern pine.

Experimental

Wood

One-half cord each of plantation-grown slash and loblolly pines was cut August 4, 1965, in Oktibbeha County, Miss., and barked. When received at the Forest Products Laboratory 2 months later, the wood was racked outdoors for a period of storage. A bolt from each species was selected a month later, chipped, and found to contain blue stain and to have but 18 percent moisture content. The rest of the pile was undisturbed until March 1966.

For preliminary digestions, four logs of each species were selected as being representative of the shipment and as affording equal volumes of slash and loblolly pines. The eight logs ranged from 7.0 to 8.5 inches in diameter. The average specific gravity was almost identical, but the slash pine, a few years older, had grown more slowly, and contained more heartwood (table 1). The average area of heartwood was low at 6 percent. The wood was reduced to nominal 9/16-inch chips with a 2-knife, 47-inch chipper of conventional design.

Cooking Procedures

Cooking liquor was prepared by absorbing sulfur dioxide in water and adding magnesium hydroxide to give equal parts of free and combined sulfur dioxide by the Palmrose method of analysis. By adding 1 part glycerin to 20,000 parts liquor and by keeping the liquor under nitrogen, the liquor was stable during the 12 preliminary digestions. The first seven digestions were at a high, 5 to 1, liquor-wood ratio and the remaining five at a low, 2 to 1, ratio (table 2).

The first seven of the preliminary digestions were made in an 0.8-cubic-foot stationary digester; the other five in an 0.8-cubic-foot tumbling digester because of the small amount of free liquor available at the lower liquor ratio. Sulfur dioxide gas was relieved from the digesters only when needed to keep the pH of the cooking liquor from going below 2.9.

In these digestions, the cooked pulp was dumped. The low-yield pulps (table 2, all but 2290y and 2288y of the preliminary digestions) were dispersed at low consistency with a propeller driven at moderate speed, put through a 10-cut flat screen, and given the TAPPI standard beater test. The two high-yield digestions (table 2, 2290y and 2288y), in which the material retained its chip form, were fiberized in a disk mill

Table 1.--Physical properties of four slash and four loblolly pine logs used for preliminary pulping investigations

Species	Average diameter	Specific gravity[1]	Age	Growth rate	Amount of heartwood
	In.		Yr.	Rings per inch	Pct.
Slash pine	7.55	0.460	22.5	6.00	10.1
Loblolly pine	7.77	.458	18.5	4.73	1.8

[1] Ovendry weight, green volume basis.

Table 2.--Preparation of magnesium bisulfite pulps from equal parts of slash and loblolly pines (shipment 5145)[1]

Digestion No.	Amount of sulfur dioxide applied[2]	Liquor to wood ratio in digester	Maximum temperature	Time at maximum temperature	Spent liquor pH	Spent liquor Sulfur dioxide content	Screenings[2]	Total yield[2]	Kappa number	Brightness before bleaching[3]
	Pct.		°C.	Hr.:min.		G. per l.	Pct.	Pct.		Pct.
DIGESTIONS AT HIGH (5 TO 1) LIQUOR-WOOD RATIO										
2286y	20.7	5.0:1	[4]165	3:00	2.36	7.4	1.7	47.4	16	51
2305y	12.1	5.0:1	165	3:10	[5]2.90	1.7	5.5	49.2	29	45
2289y	20.7	5.0:1	165	2:25	[5]2.93	12.2	3.0	50.9	31	48
2287y	20.8	5.0:1	165	2:00	[5]2.75	14.6	3.7	53.5	40	46
2298y	16.2	5.0:1	165	1:55	[5]2.98	10.4	8.7	56.3	64	41
2290y	13.8	5.0:1	160	1:55	2.93	12.2	(6)	62.4	114	40
2288y	10.4	5.0:1	160	1:20	3.08	9.5	(6)	70.9		40
DIGESTIONS AT LOW (2 TO 1) LIQUOR-WOOD RATIO										
2293y	[7]18.2	2.7:1	165	2:25	[5][5]2.93	8.2	1.8	49.0	24	48
2303y	[7]11.7	1.9:1	165	2:15	[5]2.93	6.0	3.0	50.9	34	46
2299y	[7]14.7	1.9:1	165	1:50	[8]2.05	[8]11.8	2.8	52.3	35	46
2297y	[7]17.0	2.2:1	165	1:30	2.92	19.3	3.4	56.0	54	43
2304y	[7]9.5	1.9:1	165	1:55	2.88	3.5	5.6	54.5	52	42
PULP PREPARED FOR PAPER MACHINE										
5687-92I	17.7	5.0:1	165	2:30	(9)	(10)			31	

[1] Chips lightly steamed, digester filled with liquor, 170 p.s.i. nitrogen gas applied for 10 minutes, excess liquor removed, 90 minutes to maximum temperature.

[2] Calculated on wood.

[3] Determined by Elrepho tester.

[4] 2 hours to maximum temperature.

[5] Gas relieved to hold pH (25° C.) above 2.90.

[6] Semichemical pulp.

[7] held 30 minutes at 120° C., 150 p.s.i., before removing excess liquor, 45 minutes to 165° C.

[8] pH 2.97, 10.6 g. per l., after 90 minutes at 165° C.

[9] 7.92-3.09, range of six digestions.

[10] 5.2-6.3, range of six digestions.

fitted with No. 18034 plates, and portions were given a second pass through the mill to obtain a variety of freenesses for strength evaluation. TAPPI testing methods were used where applicable.

Pulp for the paper machine was cooked in a 13-cubic-foot tumbling digester, and the cooked chips blown. The pulp passed through a 12-cut flat screen followed by a 6-inch centrifugal cleaner. Cleaner rejects were recycled once.

Discussion

Cooking Procedures

The 5 to 1 liquor-wood ratio shown for most of the digestions in table 2 is typical of ratios for batch digestion used commercially. A pulp of 16 kappa number was prepared without decomposition of the cooking liquor. A pulp of 24 kappa number was made at the lower liquor-wood ratio of 2 to 1, and, because there was no sign of decomposition, it is likely that cooking could have continued successfully to lower kappa numbers.

Advantages claimed for cooking at a low liquor-wood ratio include use of less steam, fewer screening rejects, less carbohydrate loss, faster cooking, and smaller volumes of spent liquor to be processed. The data here, however, show no benefit in yield or strength at the lower liquor-wood ratio, probably because conditions chosen for the higher ratio digestions gave adequate penetration of chemical into the chips or because impregnation at the lower ratio was not uniform

Table 3.--Properties of southern pine magnesium bisulfite pulps[1]

Digestion No.	Kappa number (unbleached)	Burst factor at freeness of--			Tear factor at freeness of--			Breaking length at freeness of--			Double folds at freeness of--			Sheet density at freeness of--			Beating time at freeness of--	
		Unbeaten	600 ml.	300 ml.	Unbeaten	600 ml.	300 ml.	Unbeaten	600 ml.	300 ml.	Unbeaten	600 ml.	300 ml.	Unbeaten	600 ml.	300 ml.	600 ml.	300 ml.
								M.	M.	M.	No.	No.	No.	G. per cc.	G. per cc.	G. per cc.	Min.	Min.
BLEACHED PULPS COOKED AT HIGH (5 TO 1) LIQUOR-WOOD RATIO																		
2286y	16	19	45	51	165	81	66	3500	7400	8300	15	115	600	0.60	0.70	0.76	12	24
2305y	29	21	46	48	138	82	74	4200	7800	8800	38	300	700	.63	.70	.75	10	20
2289y	31	26	48	54	136	77	67	4800	8200	9100	40	410	580	.61	.71	.76	16	37
2287y	40	29	49	56	133	83	72	5400	8000	9100	80	370	630	.64	.69	.76	12	27
2298y	64	25	52	60	159	84	78	4300	8500	9600	30	380	750	.61	.68	.76	12	26
BLEACHED PULPS COOKED AT LOW (2 TO 1) LIQUOR-WOOD RATIO																		
2293y	24	21	39	47	117	72	62	3900	7300	8300	15	140	200	.60	.70	.75	9	18
2303y	34	24	42	47	112	76	64	4700	7100	8100	29	230	280	.62	.70	.75	8	15
2299y	35	21	42	50	125	67	59	4100	7700	8800	22	180	460	.60	.72	.75	12	27
2297y	54	28	47	56	126	86	65	5100	8000	9000	61	240	440	.65	.69	.75	8	19
2304y	52	26	46	48	119	79	66	4800	8000	8500	45	260	380	.64	.70	.75	8	16
BLEACHED PULP FOR PAPER MACHINE RUNS																		
.....	31.0	27	43	51	137	90	72	4300	7300	8500	.....	.....	.....	.65	.71	.76	7	16
UNBLEACHED PULPS																		
2286y	16	24	45	53	137	90	80	5300	8000	9100	62	330	570	.57	.67	.72	10	18
2299y	35	30	42	47	110	82	73	6300	8000	8600	81	260	360	.58	.65	.70	9	17
2290y	114	45	44	45	103	96	85	7400	7500	7700	140	150	210	.56	.56	.61	(2)	.....
2288y	.....	30	36	35	96	89	82	5700	6600	7000	60	80	92	.48	.54	.56	(2)	.....
BLEACHED KRAFT PULP																		
4727x	39	31	72	84	288	146	114	5300	9900	11500	130	830	1250	.59	.67	.73	20	43
BLEACHED COMMERCIAL SPRUCE ACID SULFITE PULPS																		
[3]4892	.....	16	35	50	145	97	73	3800	6700	8900	.....	.....	.....	.64	.71	.81	11	37
[3]4780	.....	37	62	72	145	87	72	6100	7800	9900	.....	.....	.....	.73	.79	.89	5	17

[1]Results obtained by TAPPI standard beater test, except for 2290y and 2288y, which were fiberized and refined in a 12-inch disk refiner.
[2]Disk refiner.
[3]Shipment number.

(tables 2 and 3). Use of a stationary digester for the higher liquor–wood ratio digestions and a tumbling digester for the lower ratio digestions may have influenced the difference shown in cooking times, inasmuch as temperatures were not read at the same point in the two systems.

To insure against depletion before cooking was completed, generous amounts of chemical were charged in the preliminary digestions. Large concentrations of sulfur dioxide in the spent liquor show the amount was excessive in some cases. A moderate excess is desirable for some products because, it has been reported (6), this gives brighter pulp and more pulp at a given level of bleach requirement, whereas minimum amounts tend to improve tearing resistance of the pulp at some expense to breaking length. Comparison of 2305y and 2289y in table 2 (12.1 versus 20.7 percent of sulfur dioxide) shows that the smaller amount of chemical caused slower cooking, somewhat lower brightness, and no significant difference in yield allowing for the difference in kappa number. Table 3 shows a slight gain in the tear factor for 2305y with the smaller amount of sulfur dioxide.

Screening Rejects

Compared with commercial experience in the sulfite pulping of northern coniferous woods, the amount of rejects in the pine bisulfite pulps was large for a given kappa number. This may in part be attribute d to the preparation of the chips because the wood was unusually dry and not all of the oversized material was removed in screening. This may also be attributed in part to the species because the high content of resins in southern pine could interfere with uniform penetration of the cooking liquor,

Blue Stain

Considerable blue stain was found when the bolts of wood were sawed longitudinally for chipping. Heavy infestation does not affect yield or pulp strength, but it does reduce brightness. A hypochlorite stage in bleaching was required to remove the dark blue stain specks from the pulp. Since blue stain develops rapidly in cut wood, it can only be avoided by cooking the material promptly after cutting.

Pitch

Pitch is recognized as a problem in handling sulfite pulps made from pine. Subtle changes convert the pitch to a harmless nondepositable form if the wood is stored for some months. This favorable effect has been attributed (2, 3) to the development of additional hydrophilic groups on the surface of the resin particles as the result of oxidation, and to the hydrolysis of esters possibly involving the enzymatic system of the parenchyma, cells. However, during air-drying, micro-organisms such as blue stain fungi attack the pine wood rapidly when it is stored under warm, moist conditions.

Other means of reducing pitch deposits are available, including modification of the cooking conditions, removal of fines by screening, and extraction by caustic soda applied either to the unbleached pulp or during the bleaching sequence. Tall oil, manufactured from the fine parenchyma cells and the resin particles separated by screening or from the spent alkaline extraction liquors, offers a possible source of revenue from the pitch.

These experimental data furnish no estimate of the likelihood of pitch trouble in the mill because the paper machine runs were too brief for appreciable accumulation of pitch. There was no evidence of an objectionable sticky form of pitch in the course of cooking, bleaching, or paper-making, although microscopical examination of pulp showed considerable pitch, and hard deposits were noted in the digesters. Storage of the wood before cooking, caustic extraction in bleaching, and the use of a sidehill screen on the unbleached pulp used in making board also helped prevent problems from pitch.

Brightness and Bleaching

Largely because of blue stain, the unbleached pulps of these southern pines were not as bright as pulps of northern conifers; the pulp brightness ranged from 51 percent at 16 kappa to 41 percent at 64 kappa, For the two semichemical pulps (table 2, 2290y and 2288y), brightness was 40 percent, A good northern sulfite pulp has a brightness of 60 percent. Although southern pine would probably be used predominately as bleached pulp, some outlet would be possible in products such as newsprint and tablet if the unbleached pulps could be readily brightened.

A few trials with single applications of chemical produced 1 i mite d improvement in brightness (table 4). Brightness of 64 percent was obtained with a pulp of 35 kappa with either sodium hypochlorite or hydrogen peroxide using a rela-

Table 4.--Single-stage brightening of southern pine magnesium bisulfite pulps

Reagent	Amount[1]		Reaction conditions			Final pH	Brightness[3]
	Applied[2]	Consumed[2]	Temperature	Consistence	Duration		
	Pct.	Pct.	°C.	Pct.	Min.		Pct.
KAPPA NUMBER 64--UNBLEACHED BRIGHTNESS, 40.6 PERCENT[4]							
Sodium hypochlorite	4.0	4.0	37	10	60	.....	41.1
Hydrogen peroxide	.4	.3	70	13	240	.....	48.3
KAPPA NUMBER 35--UNBLEACHED BRIGHTNESS, 45.9 PERCENT[5]							
Sodium hypochlorite	3.0	3.0	37	10	45	10.2	48.7
Sodium hypochlorite	5.0	5.0	37	10	120	9.8	59.7
Sodium hypochlorite	7.0	7.0	37	10	150	8.8	63.6
Hydrogen peroxide	.24	.24	75	13	120	9.8	52.7
Hydrogen peroxide	.48	.43	75	13	300	8.8	58.6
Hydrogen peroxide	1.00	.99	75	10	300	9.3	64.9

[1] Sodium hypochlorite calculated to available chlorine; caustic soda added to maintain alkalinity. Hydrogen peroxide calculated to hydrogen peroxide; reagent also included 3 percent sodium silicate, 1 percent caustic soda, and 0.05 percent magnesium sulfate calculated on the pulp.

[2] Calculated on wood.

[3] Determined by Elrepho tester.

[4] Digestion 2298y.

[5] Digestion 2299y.

Table 5.--Bleaching of southern pine magnesium bisulfite pulps

Digestion No.	Kappa number	Chemicals[1]								Brightness[3]		Estimated yield[4]
		Chlorination		Caustic soda extraction		Sodium hypochlorite[2]		Chlorine dioxide		Before: last stage	After: last stage	
		Amount applied	Amount consumed	Amount applied	Terminal pH	Amount applied[5]	Amount consumed	Amount applied[6]	Amount consumed	Reaction time				
		Pct.	Pct.	Pct.		Pct.	Pct.	Pct.	Pct.	Hr.	Pct.	Pct.	Pct.
2286y	16	3.5	3.4	2.0	12.3	1.5	1.1	0.19	0.19	3	84.1	90.1	44.7
2305y	29	5.7	5.5	2.0	11.6	1.5	1.2	.19	.19	2.5		90.8	
2289y	31	5.8	5.5	2.0	12.1	1.8	1.3	.40	.40	1	86.2	87.8	46.4
2287y	40	7.3	7.0	2.0	12.0	2.0	1.5	.10	.10	2	85.1	88.3	47.7
2298y	62	12.0	11.6	2.0	11.3	2.0	1.8	.57	.57	5		89.5	47.2
2293y	24	5.2	5.0	2.0	11.4	1.6	1.2	.10	.10	1.5	83.4	87.9	45.3
2303y	34	6.3	6.1	2.0	11.2	1.5	1.1	.19	.19	4		87.4	46.1
2299y	35	6.5	6.3	2.0	11.1	1.8	1.5	.57	.45	5		89.8	47.2
2297y	54	10.0	9.8	2.0	11.4	2.0	1.8	.57	.57	5		88.9	48.2
2304y	52	10.0	9.7	2.0	11.6	2.0	1.5	.38	.32	5		90.2	47.2
2300y	46	8.6	8.4	2.0	11.4	2.0	1.7	.57	.57	5		91.0	43.2
75687-92I-1	31	6.5	6.3	2.0	11.5	1.4	1.1					90.0	
-2	31	6.5	6.3	2.0	11.4	.9	.9					87.7	
4727x[8]	39	7.5	7.4	2.0	11.2			.83	.83	1.5			
				1.0	11.4			.57	.54	5		87.3	43.7

[1] Bleaching conditions: Consistence of 2 percent for chlorination, of 10 percent for caustic soda extraction, sodium hypochlorite, and chlorine dioxide stages. Temperature of 25° C. for chlorination, 70° C. for caustic soda, 37° C. for sodium hypochlorite, and 75° C. for chlorine dioxide stages. Duration of chlorination and caustic soda both 1 hour; sodium hypochlorite, 5 hours. All chemicals calculated on weight of unbleached pulp.

[2] Caustic soda added to maintain alkalinity, terminal pH 10. 2-10.4.

[3] Determined by Elrepho tester.

[4] Calculated on wood.

[5] Calculated as available chlorine.

[6] Calculated as available chlorine dioxide.

[7] Combined pulps bleached in two batches.

[8] Kraft pulp, five stages of bleaching; chlorine, caustic soda, chlorine dioxide, caustic soda at 50° C., and chlorine dioxide.

tively high dose of chemical. Pulp of higher kappa number was more resistant,

Brightnesses of 87 to 91 percent followed successive application of chlorine, caustic soda, sodium hypochlorite, and chlorine dioxide to the pulps from the small-scale digestions (table 5). With the fourth stage omitted, brightnesses were between 84 and 86 percent. Ordinarily a well-cooked sulfite pulp can be bleached to high brightness with chlorine-caustic extraction-chlorine dioxide, but, as mentioned, hypochlorite was needed to eliminate the blue stain. At the Laboratory, bleaching chemicals are utilized more effectively in large-scale than in small-scale applications. Accordingly, in preparing pulp for the paper machine, adequate brightness was obtained in three stages,

Yields and Pulp Properties

Yield differences between pulps were much less after bleaching than before bleaching; this showed that most of the yield advantage in stopping the digestion at high kappa number was lost (tables 2 and 5). Such loss is expected because differences in unbleached yield are largely lignin, which is removed in bleaching. However, net gains of 3 or 4 percent, wood basis, followed if cooking was stopped at 65 instead of 25 kappa. The advantage of the gain is partly

offset by higher bleaching costs, but the pulps were also stronger if cooking was stopped at 30-plus kappa instead of 20, which is about average for the several grades of acid sulfite pulp cooked for bleaching.

Evaluation of Pulps

In strength, the pine pulps generally fell between the two commercial spruce acid sulfite pulps shown in table 3. Two spruce reference pulps were included rather than one to suggest the rather wide range of physical properties among commercially used sulfite pulps.

The TAPPI standard sheets made from the pine pulps were lower in density than were those from the spruce pulps, particularly shipment 4780; this reflected the high stiffness and resilience of thick-walled southern pine fibers. Fundamentally, low-density sheets must be low in strength because the number of fiber-to-fiber bonds holding the sheet together must be fewer. It will be noted that sheets from the stronger spruce pulp were also considerably denser. Within limits, low density can be corrected in the mill by increasing pressure on the web.

The unbleached semichemical pulps, 2288y and 2290y) were weaker than the bleached, fully cooked pulps except in tear. Sulfite pulps in this yield range have extensive use, notably as the long-fiber component in newsprint, but the low brightness in this case is a disadvantage. Although much of the low brightness can be laid to the blue stain, pine sulfite pulps show a typical yellowish cast unless they are bleached.

Paper and Board Making

Pulp for paper and board making on the Laboratory's experimental paper machine was provided by multiple digestions in the 13-cubic-foot tumbling digester following the general conditions described for digestion No. 2289y (table 2) except that the chemical charge was reduced to 17.7 percent of sulfur dioxide. Tests on cooled liquor samples taken 5 minutes before blow showed an averaged residual of 6.3 grams per liter of sulfur dioxide and a pH of 2.92. The kappa number of the composite pulp was 31.

The pulp bleached easily in three stages without need of the chlorine dioxide stage applied in the small-scale bleaches as previously described, The pulp was bleached in two batches; the first batch had a brightness of 90 after the application of 1.4 percent of chlorine as hypochlorite in the last stage of bleaching, whereas the second had a brightness of 87.7 after 0.9 percent of chlorine as hypochlorite (table 5, 5687-921).

The bleached bisulfite pulp of southern pine was used in bond, book, toweling, and tissue papers and as the top ply for linerboard. The unbleached pulp was used only as the top ply of linerboard.

Offset Book Paper

A well-formed offset paper (table 6, machine run 6601) was made from a furnish containing 30 percent experimental pine bisulfite pulp, 50 percent commercial sweetgum kraft pulp, and 20 percent commercial western softwood kraft pulp. The paper had finish, air resistance, opacity, oil penetration resistance, and tearing resistance properties equal to or higher than those of many commercially made offset papers. Its bursting and tensile strengths were not as high as some papers, but these properties could be improved with more starch surface size or additional processing of the pulp. The starch surface treatment greatly enhanced the burst and tensile strengths of the paper; without it, the paper was about 35 percent lower in these strength properties.

The entire furnish, which included 15 percent clay, 5 percent titanium, and 1 percent rosin size, was processed in the conical refiner to a freeness of about 470 milliliters.

Coating-Base Papers

For the experimental coating-base papers (table 6, machine run 6603) the furnish consisted of 40 percent bleached pine bisulfite pulp and 60 percent bleached gum kraft pulp. The furnish for the 32-pound magazine base had 7 percent clay filler, whereas that for the 45-pound book base had 10 percent. The gum portion was refined in the conical refiner to 270 milliliters freeness and then blended with the bisulfite pulp with no further refining.

Although actual coating trials would be needed before the full value of the bisulfite pulp for

Table 6.--Properties of bond and printing papers with bleached magnesium bisulfite pulp from southern pine in the furnish[1]

Machine run No.	Stuff freeness (Canadian Standard)	Sheet properties[2]																
		Weight		Thickness	Density	Bursting strength	Internal tearing resistance		Folding endurance	Tensile strength		Air resistance	Castor oil penetration	Smoothness (Bekk)	Brightness	Opacity	Ash content
		Trade size	Square meter				Machine direction	Cross-direction	M.I.T. (Av. two directions)	Machine direction	Cross-direction						
	Ml.	Lb.	G.	Mils	G. per cc.	Pts.	G.	G.	Double folds	Lb. per in. width	Lb. per in. width	Sec. per 100 cc.	Sec.	Sec.	Pct.	Pct.	Pct.
NOMINAL 20-POUND BOND, 17 BY 22 INCHES, 500-SHEET																		
3,4 6602	400	19.9	74.8	3.36	0.88	17.6	44.0	46.0	16	24.6	9.3	16	155	45	83.8	82.5	11.2
3 6600	360	20.0	75.3	3.53	.84	17.0	43.2	48.8	13	21.9	9.0	90	114	32	84.4	85.2	7.9
5,6 6605	410	17.7	66.6	3.31	.79	19.8	31.4	33.0	23	23.9	11.6	6	30	34	84.7	77.8	7.6
NOMINAL 50-POUND OFFSET BOOK, 25 BY 38 INCHES, 500-SHEET																		
4,7 6601	470	49.7	73.5	3.20	.90	18.2	41.0	46.6	13	22.5	10.0	26	76	76	88.5	91.1	15.8
7 6601A	470	49.6	73.2	3.34	.86	12.1	45.4	56.4	7	16.8	6.3	26	56	57	89.0	92.9	16.6
NOMINAL 45-POUND BOOK COATING-BASE STOCK, 25 BY 38 INCHES, 500-SHEET																		
6 6604	.....	45.0	66.6	3.34	.79	16.0	36.4	45.2	15	22.2	7.6	17	57	33	85.6	82.5	9.0
NOMINAL 32-POUND MAGAZINE COATING-BASE STOCK, 25 BY 38 INCHES, 500-SHEET																		
6 6603	260	32.8	48.6	2.48	.77	12.7	22.6	29.8	15	16.0	5.9	20	61	38	84.9	75.5	6.0

[1] All furnishes contained 1.0 percent rosin size. In addition, the bond and 45-pound coating-base furnishes had 10 percent clay, the offset book furnish, 15 percent clay and 5 percent titanium dioxide, and the 32-pound coating-base furnish, 7 percent clay.

[2] Tested according to TAPPI methods except for brightness determined with the Elrepho tester.

[3] Bleached pulp furnish consisted of 100 percent southern pine magnesium bisulfite pulp.

[4] Surface-sized at horizontal size press using a 9.0 percent concentration of medium-viscosity ethylated cornstarch.

[5] Bleached pulp furnish consisted of 50 percent southern pine magnesium bisulfite pulp and 50 percent sweetgum kraft pulp.

[6] Bleached pulp furnish consisted of 40 percent southern pine magnesium bisulfite pulp and 60 percent sweetgum kraft pulp.

[7] Bleached pulp furnish consisted of 30 percent southern pine magnesium bisulfite pulp, 50 percent sweetgum kraft pulp. and 20 percent western softwood kraft pulp.

coating papers could be determined, it would appear that these experimental papers would be suitable coating-base stock. They had good strength properties, smoothness, air resistance, oil resistance, and opacity (table 6), and these were in the range commonly noted for similar weight coating-base papers manufactured commercially.

Bond Papers

The experimentally made bond papers had good surface finish, but their strengths fell in the low range of many commercially manufactured bond papers. The two papers (table 6, machine runs 6600 and 6605) with blends of the pine bisulfite and gum kraft were well formed, whereas the paper made with 100 percent pine bisulfite pulp was not so well formed. This paper had better tearing resistance than the sheet containing 60 percent hardwood pulp, but it did not have as high burst or tensile strengths. The bisulfite pulp in this mixture was not refined to maintain more of its initial tearing resistance, whereas the sweetgum pulp was refined in the conical refiner to about 270 milliliters freeness. In the run with 100 percent bisulfite pulp, the refining was accomplished using the conical refiner to reduce the freeness to 400 milliliters.

The paper containing equal parts of the bisulfite pulp and the gum pulp had strength properties similar to the paper made with 100 percent bisulfite pulp. This sheet had no surface size. Had starch been applied to the surface, the burst and tensile strengths would have undoubtedly been higher, For this paper the two pulps were refined together in the conical refiner.

Tissue Papers

The two experimental 12-pound facial tissues and the one 14-pound toilet tissue made with a furnish containing 80 percent bisulfite pulp (table 7) were equal to or better in strength, stretch, and absorbency than those of "weigh" sheets of each grade taken from a commercial paper machine. These tissues were not quite as soft as the commercially made tissues. The stock for these was refined in the jordan to freenesses of 570 milliliters for the facial tissues and 610 milliliters for the toilet tissues. With less processing the softness could be improved at the sacrifice of the excess tensile strength.

All the tissues were dry creped at 92 to 94 percent solids, with 0.1 percent animal glue added for better adhesion to the creping dryer,

Table 7.--Properties of creped sanitary tissue and toweling papers using bleached magnesium bisulfite pulp from southern pine in the furnish[1]

Machine run No.	Fiber furnish: Southern pine bleached magnesium bisulfite	Fiber furnish: Gum bleached kraft	Stuff freeness (Canadian Standard)	Weight: Trade ream, 14 x 36 - 500	Weight: Square meter	Thickness[2]	Bursting strength	Tensile strength[3]: Machine direction	Tensile strength[3]: Cross-machine direction	Tensile strength[3]: Average, both directions	Stretch: Machine direction	Stretch: Cross-machine direction	Water absorbency[4]	Softness (Clark): Machine direction	Softness (Clark): Cross-machine direction	Softness (Clark): Overall	Brightness
	Pct.	Pct.	Ml.	Lb.	G.	Mils	Pts.	Lb. per in. width	Lb. per in. width	Lb. per in. width	Pct.	Pct.	Sec.				Pct.
NOMINAL 12-POUND FACIAL TISSUE[5]																	
6613B	80	20	610	12.9	21.0	2.68	2.0	0.92	0.88	0.90	23.4	3.9	6.4	317	76	156	82.4
6613B	80	20	610	12.7	20.7	2.47	2.1	.95	.90	.92	20.1	4.2	11.8	353	95	183	81.9
NOMINAL 14-POUND TOILET TISSUE[5]																	
6614	80	20	610	17.2	28.0	4.0	3.1	1.67	1.47	1.57	18.8	3.8	6.4	130	40	72	82.7
NOMINAL 30-POUND TOWELING, WET STRENGTHENED[6]																	
6612	70	30	565	30.9	50.4	6.0	7.2	5.7	5.4	5.6	8.9	2.2	37	12.6	5.6	8.4	80.7

[1] Except for brightness determined by the Elrepho tester, testing was by TAPPI methods with softness calculated by using thickness of creped specimen.

[2] Crep not removed.

[3] The wet tensile strength determined with the Finch attachment was 1.49 pounds per inch width for the machine direction and 1.27 pounds per inch width for the cross-machine direction; the average was 1.38 pounds per inch width and resulted in an average of 25.1 percent strength retained.

[4] 0.01-milliliter drop was used for sanitary tissues and a 0.1-milliliter drop for toweling.

[5] Creped at a web solids of 92 to 94 percent. Furnish contained 0.1 percent animal glue added continuously.

[6] Creped at a web solids of 35 percent. Furnish contained 0.25 percent polyamide resin added continuously. Sheets were heat-treated for 1 hour at 105° C. and then conditioned at 73° F. and 50 percent relative humidity before testing.

Toweling Paper

A creped toweling paper with properties better than those specified in Federal Specification UU-T-591d was made with a furnish of 70 percent pine bisulfite pulp and 30 percent commercial sweetgum kraft pulp. Compared with unembossed wet-strengthened t ow e l papers made commercially, the dry and wet tensile strengths of the experimentally made towel. were higher. However, the towel was not as soft or as absorbent. These properties could be improved with less processing but this would result in a reduction of the excess tensile strength. The refining was done in the jordan. The experimental towel paper had 0.25 percent of a polyamide resin added continuously to the pulp furnish. It was creped at about 35 percent solids.

Linerboard

Forty-two pound linerboards of good quality were made with both the unbleached and the bleached bisulfite pulps as the top ply (table 8). These boards had strengths, including edgewise compressive resistance, equal to or better than southern kraft boards made commercially. In these runs the top ply of bisulfite pulp constituted about 22 percent of the weight of the board with the bottom ply made from 100 percent commercially prepared unbleached southern pine kraft pulp, The kraft pulp was refined in a double-disk mill to 600 milliliters and the bisulfite pulps to about 450 milliliters freeness in the conical refiner.

The bleached bisulfite pulp did not completely mask the unbleached kraft base. The board surface, although smooth, had a "mottled" appearance similar to the common No. 3 white mottle kraft liner. It should provide a good printing surface. The unbleached bisulfite pulp had a gray cast as did the board made from it. The pulp had been washed prior to refining on a sidehill screen to remove the dark fines. This resulted in a somewhat lighter pulp, but did not completely eliminate the grayness.

Both linerboards were evaluated for resistance to cracking when bent along a score line. Compared with two experimental all-kraft liners, the two with the bisulfite pulps exhibited more cracks in the surface. This is typical of bisulfite-made boards because of their tighter and better bonded characteristics.

Table 8.--Evaluation of linerboards with the bisulfite pulps as the top ply[1]

Property	Machine run No. 6625[2]	Machine run No. 6626[2]
Weight - 1000 square feet.....lb.	43.4	42.6
- square meter.....g.	212	208
Thickness.....mils	9.9	9.4
Density.....g. per cc.	.84	.87
Bursting strength.....p.s.i.	103.4	111.5
Internal tearing resistance		
Machine direction.....g.	342.4	337.6
Cross-machine direction.....g.	372.8	381.0
Tensile strength		
Machine direction.....lb. per in. width	92.3	87.1
Cross-machine direction....lb. per in. width	46.7	46.0
Folding endurance		
Machine direction.....double folds	1500	2073
Cross-machine direction.....double folds	1239	1484
Edgewise compressive resistance		
Machine direction.....lb.	122	119
Cross-machine direction.....lb.	94	95
Air resistance.....sec. per 100 cc.	73	126

[1] Tested according to TAPPI methods. Specimens for compressive resistance measured 1/2 inch by 6 inches instead of 1/2 inch by 2 inches as specified in T 472 for boards having a thickness less than 20 mils.

[2] The top ply, which constituted 22 percent of the board weight, consisted of the unbleached pine bisulfite pulp (digestions 5687I-56921) in machine run 6625 and bleached bisulfite pulp (bleach 6529) in machine run 6626. These pulps were applied with a secondary headbox. The base sheet in both runs consisted of a commercial southern pine kraft pulp.

Conclusions

Bleachable sulfite pulps can be made from slash and loblolly pines without liquor decomposition if a magnesium bisulfite cooking liquor is used. A brightness of about 90 percent can be obtained in three stages of bleaching. Discoloration from blue stain organisms in the wood is removed if a hypochlorite stage is included. Unbleached blue-stained southern pine pulp can be brought to the 60 percent brightness level of northern sulfite pulp by single applications of hypochlorite or peroxide, but the chemical requirement can be high.

No sticky pitch deposits were noted under favorable experimental conditions that included the use of wood stored outdoors. The likelihood of pitch troubles can be accurately estimated only by a mill run of greater length.

The pine pulps were not consistently stronger or weaker than the spruce acid sulfite pulps, but these southern pine pulps should be competitive with northern coniferous pulps wherever the coarser nature of southern pine fiber is not objectionable.

Linerboard, toweling, bond, printing, and tissue papers from southern pine sulfite pulp, made on the Laboratory's paper machine, were generally of good commercial quality.

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