TABLE 2. *Classification of observed bands in chlorofluoromethane*

Assignment	Intensity	Wave-length	Wave number (vacuum)
		μ	cm^{-1}
ν_4	M	26.0	385
ν_3	VS	13.16	760
ν_9	M	9.99	1,001
ν_7	VS	9.36	1,068
ν_5	M	8.09	1,236
ν_8	S	7.40	1,351
ν_2	W	6.78	1,475
$\nu_8+\nu_7$	M	4.725	2,115
$\nu_2+\nu_7+2\nu_5$	VW	4.141	2,414
$\nu_2+\nu_8$	VW	3.544	2,821
$2\nu_2$	M	3.434	[a] 2,911
ν_1	MS	3.340	[a] 2,993
ν_6	M	3.280	[a] 3,048
$3\nu_7$	VW	3.184	3,140
$\nu_1+\nu_7$	VVW	2.4841	4,025
$\nu_6+\nu_7$	VW	2.4719	4.044
$\nu_1+\nu_3+\nu_4$	VVW	2.4622	4,060
$\nu_6+\nu_3+\nu_4$	W	2.4356	4,105
$\nu_6+\nu_5$	W	2.3456	4,262
$\nu_8+\nu_6$	VW	2.3021	4,343
$\nu_1+\nu_2$	M	2.2865	4,372
$\nu_2+\nu_6$	MS	2.2291	4,485
$\nu_1+\nu_5+\nu_2$	VVW	1.7880	5,591
$2\nu_8+\nu_6$	VW	1.7553	5,695
$2\nu_2+\nu_1$	VW	1.7169	5,823
$2\nu_1$	M	1.7005	5,879
$\nu_1+\nu_6$	W	1.6818	5,944
$2\nu_6$	MS	1.6572	6,032

[a] Raman value.

is the only second harmonic band observed in the spectrum when the 5.0-cm cell was used and indicates that ν_7 is very intense. The first harmonic band of ν_2 is fairly intense in the infrared spectrum, and this increase in intensity is brought out by resonance with ν_1 at 2,993 cm^{-1}. In the spectrum of dichloromethane $2\nu_2$ is weak, as the conditions of resonance are not so favorable.

The resolution of some of the bands in the regions of 1.6 and 2.4μ into their rotational structures makes it possible to determine one of the moments of inertia for the molecule. The separation of the rotational lines varies slightly from one band to another. The average spacing of the lines is about 2.4 cm^{-1} in the 1.7005μ band. A study of the rotational structure of this molecule and that of dichloromethane and difluoromethane is being made and will be the subject of another report.

The spectrum of chlorofluoromethane supports the assignments of the fundamental bands made on the spectrum of dichloromethane. Further experimental work will be necessary to have sufficient data for determining the CClF angle in this molecule.

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Resin Bonding of Hardwood Fibers in Offset Papers

By Bourdon W. Scribner, Merle B. Shaw, Martin J. O'Leary, and Joshua K. Missimer

A further investigation was made of the application of resin bonding to the development of strength in offset papers made principally of short hardwood fibers that develop little strength by the conventional beating. Melamine-formaldehyde resin was used. The papers were made from hardwood pulps produced at the U. S. Forest Products Laboratory in experimental study of the pulping of aspen, black gum, paper birch, and beech. The pulps were prepared by the mechanical, sulfate, soda, sulfite, and neutral sulfite processes. By the use of the melamine resin, papers having good strength and resistance to pick, combined with low expansion and curl, were produced with very little beating. The pulps that gave the best results comprised aspen sulfate, aspen soda, aspen sulfite, birch sulfite, and black gum sulfate. Resin-bonded papers containing 75 percent of these pulps compared favorably with papers made in the conventional way with the usual 50 percent of commercial hardwood fibers. An appreciable increase in the proportion of hardwood fibers used in offset papers would greatly extend pulpwood resources.

I. Introduction

Effective utilization of large quantities of hardwoods is an outstanding pulpwood problem. The pulp and paper industry has had an amazing growth during this century, but the supply of the more generally used pulp woods is steadily decreasing. Wood is the most important source of paper-making material. Pulp produced from coniferous or needle-leaved trees (softwoods), such as spruce, fir, and pine, is used to a much greater extent than that produced from the hardwood or broad-leaved trees, such as the various "poplars", birch, beech, gum, etc., commonly used for pulping. The use of hardwoods for pulping is good forestry practice, and in regions having a large volume of hardwood species or inferior trees unsuited for lumber or similar products is an economic necessity.

In comparison with spruce and other softwoods, however, the use of hardwoods has been limited by the characteristics of the hardwood fibers. The characteristics that affect the manufacture of paper vary in kind and quantity with different woods. One differentiation is the length of fiber, which is approximately from 1 to 1.5 mm for hardwoods and from 2.5 to 4.5 mm for coniferous wood. The fiber of the hardwood trees also has a structure that is different from that of the conifers. Its soft and absorbent texture renders it useful for bulky papers such as certain classes of printing paper, but it is not as strong as the softwood fiber.

The strength of paper depends on the strength of its fibers and on the adhesive bond between them. Cellulose is a colloid. It gelatinizes ("hydrates") on beating it in water and thus causes gel-like bonds to be formed between the fibers of the finished sheet.

Because of the large increase in external surface (fibrillation) produced by beating, the number of contacts and subsequent bonds is greatly increased, thereby increasing the strength of the paper. The hardwoods do not develop good bonding quality to the extent that conifers do.

The development of strength by beating the fibers tends to affect adversely some properties needed for good printing quality. Chief among these are high opacity, good oil absorption, high permeability to air, low expansivity, and low curl. Low expansion and contraction are particularly important in lithographic offset papers for good register of successive color prints, as in printing maps that may be run through the press as many as 15 times. Hardwood pulps have all the properties needed for good offset printing paper except strength.

An investigation at the Bureau during World War II resulted in the development of offset lithographic paper for war maps having great strength imparted by melamine-formaldehyde resin bonding and excellent printing quality.[1] A subsequent investigation of melamine-formaldehyde resin in papers made from various mixtures of a commercial softwood pulp and two commercial hardwood pulps showed that the proportion of the latter could be largely increased without impairment of the strength of the papers, and with improvement of their printing quality, thus permitting increased use of hardwood fibers.[2]

The investigation reported herein is an extension of such study of hardwood pulp to pulps produced experimentally from different species of woods at the U. S. Forest Products Laboratory, in a study of application of the various commercial pulping processes to hardwoods.

II. Experimental Paper-Making Equipment

The paper-making equipment at the Bureau is semicommercial in size and is adapted to the experimental manufacture of papers under conditions that simulate those of typical industrial plants. Detailed descriptions are contained in previous publications.[3 4 5]

The equipment used in this particular work consisted essentially of a 50-lb. beater with copper-lined tub and manganese-bronze bars and plate; a jordan refiner with bars of bronze and steel alloy; a four-plate, flat screen; a 29-in. fourdrinier paper-making machine with a wire 33 ft. in length, two presses, nine 15-inch dryers, a calender stack of seven rolls, and a reel; and a five-roll supercalender.

III. Fibrous Raw Materials

Two commercial pulps, bleached sulfite (coniferous) and bleached soda (deciduous), were used in various mixtures with the hardwood pulps prepared by the Forest Products Laboratory.

Bleached sulfite, made by cooking eastern spruce wood in a solution of calcium bisulfite, is a standard quality of pulp widely used in offset papers. It is composed of relatively long, strong fibers that hydrate rather readily with beating.

Soda pulp is a short-fibered filler-type pulp made by cooking hardwood in a solution of caustic soda. The fibers are characteristically soft and bulky and do not hydrate readily. The pulp had excellent strength for a pulp of this kind.

The hardwood pulps supplied by the Forest Products Laboratory were prepared from the following deciduous woods: Aspen, black gum (tupelo), paper birch, and beech. Also included was a coniferous pulp made from Douglas fir. The pulps were prepared by the mechanical (groundwood), sulfate, soda, sulfite, and neutral sulfite (semichemical) processes. The identification number assigned to each pulp by the Forest Products Laboratory, and their description of it follow.

Quaking Aspen Pulps

a. Unbleached free [6] groundwood pulp (item 1).—This pulp is characterized by its relatively short fiber length, low strength, and high freeness. It was prepared at a high rate of production and with low energy consumption. The energy requirement was about 40 percent that of the slower pulp described below (c).

b. Peroxide-bleached free groundwood pulp (item 2).—This pulp was bleached at a high density by a conventional single-stage sodium peroxide process to give a bright, free, low-strength, short-fibered pulp.

c. Unbleached book-grade groundwood pulp, slow (item 14).—This pulp is characterized by its low freeness, short fiber length, and fair strength. The production rate was low and the energy requirement high.

d. Bleached sulfate pulp (item 7).—A fully bleached sulfate pulp, conventionally cooked, and bleached by a three-stage, chlorination—alkali extraction—hypochlorite, bleaching process. This pulp is typical of short-fibered pulps having good strength and softness.

e. Bleached soda pulp (item 15).—This pulp was produced by the conventional soda process and bleached by a three-stage, chlorination—caustic extraction—hypochlorite, bleaching process. This short-fibered pulp was slow hydrating and relatively weak, as is typical for this kind of pulp, but was soft and bulky.

f. Bleached sulfite pulp (item 16).—This was a commercial pulp prepared by the calcium-bisulfite process and bleached by the conventional single-stage hypochlorite process. It is a weak, short-fibered pulp, typical of aspen sulfite.

g. Bleached neutral sulfite (semichemical) pulp (item 5).—The cooking process consisted of partially digesting the aspen chips with a solution of sodium sulfite and sodium bicarbonate and then

[1] J. Research NBS **37**, 325 (1946) RP1751.
[2] J. Research NBS **40**, 427 (1948) RP1887.
[3] Tech. Paper BS **21**, 338 (1927) T340.
[4] BS J. Research **3**, 904 (1929) RP121.
[5] Paper Trade J. **89**, No. 19, 60 (1929).

[6] "Free" is a term applied to fibers from which water drains rapidly because of the low hydration of the fibers. The converse term is "slow."

defibering the softened chips in an attrition mill. The pulp was bleached by a conventional multistage process including chlorination, alkali extraction, and hypochlorite treatment. A high yield of fully bleached pulp was obtained. It is characterized by fairly high strength, rapid hydration, and considerable hardness.

h. Mixed aspen and spruce bleached sulfate pulps (item 3).—Sulfate pulp was made by a conventional pulping procedure from a mixture of quaking aspen (67%) and spruce (33%) and bleached by a multistage treatment consisting of chlorination, alkali extraction, two-stage hypochlorite bleaching, and a sulfur dioxide wash. This pulp had a much lower bursting strength and a somewhat lower tearing strength than would be expected if less drastic bleaching conditions had been used. The mixture of long and short fibers in this pulp had a higher tearing resistance than the pulp made from the hardwood alone.

Black Gum (Tupelo) Pulp

Bleached sulfate pulp (item 6).—A bleachable sulfate pulp was made by a conventional sulfate pulping procedure and the pulp bleached by a multistage process involving chlorination, alkali extraction, and two-stage hypochlorite bleaching. A bright, fairly strong, and fairly soft short-fibered pulp was obtained. The bursting strength of the pulp was perhaps lower than would normally result from less drastic treatment.

Paper Birch Pulps

a. Peroxide-bleached groundwood pulp (item 8).—This pulp is very short fibered and has a correspondingly low strength. It was bleached to high brightness by a high-density single-stage peroxide process.

b. Bleached sulfite pulp (item 10).—The pulp was produced by the conventional sulfite process using calcium-base liquor. The pulp was bleached by a conventional two-stage chlorine-hypochlorite process. It is a fairly strong short-fibered pulp.

c. Bleached neutral sulfite (semichemical) pulp (item 9).—The wood was partially pulped with a sodium sulfite and sodium bicarbonate liquor, and the softened chips were then defibered in an attrition mill. The semichemical pulp was bleached by a multistage, chlorination—alkali extraction—hypochlorite, bleaching process. The fully bleached pulp was characterized by high yield, high strength, rapid hydration, and considerable hardness.

Beech Pulp

Bleached sulfate pulp (item 12).—The wood was pulped by a conventional sulfate pulping procedure. The pulp was bleached by a multistage process comprising chlorination, alkali extraction, and two-stage hypochlorite bleaching. This pulp was somewhat underbleached to give a fair brightness. The pulp is short-fibered and of fair strength.

Douglas Fir Pulp

Bleached neutral sulfite (semichemical) pulp (item 13).—A fully bleached pulp was made from Douglas fir (coniferous) by partial cooking with a sodium sulfite and sodium bicarbonate liquor followed by defibering the softened chips in an attrition mill. A fairly high yield of unbleached pulp was obtained. It was bleached by a conventional, chlorination—alkali extraction—hypochlorite, bleaching process. The pulp is characterized by its high strength, especially tearing resistance, and long fibers.

IV. Manufacturing Procedure

A series of papers was made from the pulps with and without the resin bonding. The manufacturing factors were kept as nearly constant as possible. The pulps were beaten for 1½ hr, which was considered the minimum time for satisfactory results.

Fifty pounds of pulp and 1 percent (based on weight of fiber) of resin size were used for each machine run. The beaten stock was dropped directly to a chest from which it was pumped in a continuous stream through the stuff box and the jordan refiner to the paper machine. The stuff box was of the regulating type with constant head over an adjustable orifice. The jordan was used as a mixer only, with the same setting for all papers.

The melamine-formaldehyde resin was added in the form of a colloidal solution made by dissolving the powdered resin in warm water acidified with hydrochloric acid. The solution was added continuously at uniform rate to the paper-making stock just before it entered the head box of the paper machine. The temperature of the stock at the head box was maintained at $90° \pm 2°$ F.

Melamine is a triamino derivative of symmetrical triazine consisting of a six-membered ring of alternate carbon and nitrogen atoms. It was discovered by Von Liebig in 1834 who, thinking it was the amine of melam, called it melamine. The particles of the colloidal resin have a positive charge and, since cellulose is negatively charged, they are therefore quickly adsorbed on the cellulose fiber. The heat of the paper-machine drying cylinders completes the polymerization of the resin particles, forming a water-insoluble bond between the fibers.

The finish imparted by the small paper machine calender was relatively low, therefore the papers were given light supercalendering to obtain a smoothness comparable to commercial "machine finish".

V. Sampling and Testing

The method of sampling paper from a machine run in the paper mill was as follows: The paper wound on the reel of the paper machine was slit across the web, thereby being converted into a stack of sheets. The stack was then cut so as to give an entire cross section of the sheets for sampling. The resultant stack was divided into seven parts. From the first part, 13 sheets were laid out as the first sheets of 13 packs to be built up. From the second part, 13 sheets were likewise distributed as the second sheets of the packs. From each of the seven parts respectively a sheet was added to each pack. The procedure was then repeated until all the paper had been distributed into the 13 packs. The odd-numbered (1–3–5–7–9–11–13) packs were then assembled, one above the other, to make one bundle of paper, and similarly the even-numbered packs to make another. From these bundles sheets were taken for the test samples.

All tests of the papers were made according to the Standard Methods of the Technical Association of the Pulp and Paper Industry,[7] except the air permeability test by the Carson method. This was determined with a Carson Precision Permeability Tester,[8] which measures the rate of air flow through the paper per unit of area with a pressure difference of 1 g/cm^2.

VI. Discussion of Papers and Data

The complete test data for the papers are given in table 1. Table 2 shows the consistent improvement in strength obtained with melamine resin irrespective of the kind of experimental pulping processes used. Table 3 shows that for a given pulping process, the improvement in strength by use of melamine resin was uniformly good for different species of wood.

[7] Available from the Association at 122 East 42nd Street, New York 17, N. Y. The methods specify the number of specimens for each test, as well as the other details of testing.

[8] BS J. Research 12, 567 (1934) RP681.

Figures 1 and 2 give a comparison of papers containing 75-percent experimental hardwood pulps and melamine resin, with papers made without melamine resin having the usual content of 50-percent commercial hardwood pulp. The other figures also show graphically the beneficial effects obtained with the use of the resin with various pulps. The word "blank" in the figures means that no melamine resin was added; an "M" is an abbreviation of melamine resin. Following is a discussion of the effects of melamine resin on the properties of the papers as shown by the data.

Unbleached aspen groundwood, free (item 1).—The fiber furnish for the three runs, 1492–4, was 75 percent of aspen groundwood. The tests on the papers show that the bursting strength, folding endurance, and tensile strength were all improved by the addition of melamine, the improvement being more pronounced with the greater amount of resin. The bonding resin improved also the resistance of the surface to picking, as measured by the wax test, without excessive increase in expansion of the papers or tendency to curl (fig. 3).

Malamine resin was not used in run 1498, and an equal amount of bleached aspen neutral sulfite pulp (item 5) was substituted for the sulfite (coniferous) pulp. The aspen pulp was characterized by fairly high strength, rapid hydration, and considerable hardness. The paper showed only fair bursting strength and low folding endurance, tensile strength, tearing strength and resistance to pick, although the

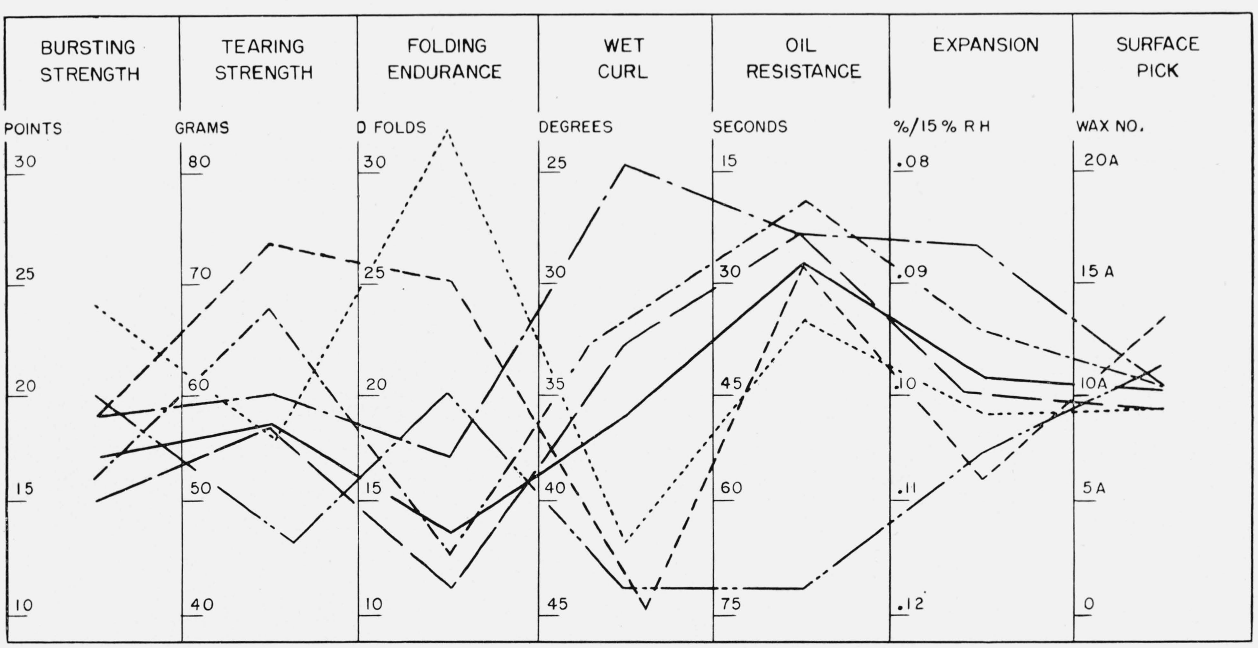

FIGURE 1. *For papers containing 1 percent of melamine resin, the physical properties of experimental papers composed of 75-percent hardwood fibers and 25-percent sulfite softwood fibers are as good as, and in some instances better than, papers composed of 50-percent commercial soda hardwood fibers and 50-percent commercial sulfite softwood fibers.*

——— 1560, 50% strong soda pulp, 50% eastern sulfite (commercial); —— —— 1538, 75% bleached aspen sulfate, 25% eastern sulfite (commercial); —— · —— 1558, 75% bleached aspen soda, 25% eastern sulfite (commercial); —— · · —— 1542, 75% bleached aspen sulfite, 25% eastern sulfite (commercial); – – – – 1516, 75% bleached black gum sulfate, 25% eastern sulfite (commercial); — · — · — 1534, 75% bleached paper birch sulfite, 25% eastern sulfite (commercial); · · · · · 1502, 40% strong soda pulp, 60% bleached sulfate (67% aspen, 33% spruce).
(All the above with 1% melamine resin.)

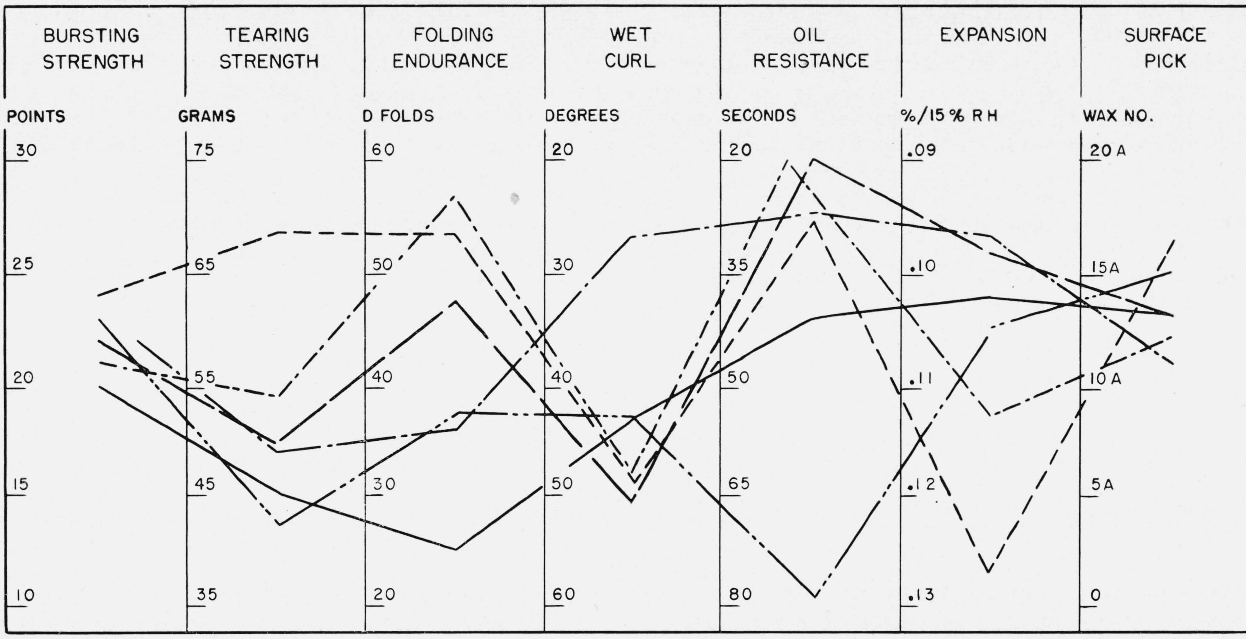

FIGURE 2. *For papers containing 3 percent of melamine resin, the physical properties of experimental papers composed of 75-percent hardwood fibers and 25-percent sulfite softwood fibers are better in most instances than the papers composed of 50-percent commercial soda hardwood fibers and 50-percent commercial sulfite softwood fibers.*

——— 1561, 50% strong soda pulp, 50% eastern sulfite (commercial); —— —— 1539, 75% bleached aspen sulfate, 25% eastern sulfite (commercial); —— · —— 1559, 75% bleached aspen soda, 25% eastern sulfite (commercial); — · · — 1543, 75% bleached aspen sulfite, 25% eastern sulfite (commercial); - - - - 1517, 75% black gum sulfate, 25% eastern sulfite (commercial); — · — · — 1535, 75% bleached paper birch sulfite, 25% eastern sulfite (commercial).
(All the above with 3% melamine resin.)

TABLE 1. *Comparative data on offset papers made from hardwood fibers bonded with melamine-formaldehyde resin*

Run No.	Pulp	Forest Products item No.	Melamine-formaldehyde resin added	Weight [1] 25 by 40 in., 500 sheets	Thickness	Bursting strength	Folding endurance (double folds) MIT (tension 1 kg): Machine direction	Folding endurance: Cross direction	Tensile strength: Machine direction	Tensile strength: Cross direction	Tearing resistance: Machine direction	Tearing resistance: Cross direction	Expansivity (15% change in relative humidity): Machine direction	Expansivity: Cross direction	Opacity (contrast ratio)	Smoothness (Bekk)	Surface pick (wax No.)	Oil penetration	Air permeability	Sizing value (dry indicator)	Curl
			Pct.	*lb.*	*Inch*	*Pts.*			*kg*	*kg*	*g*	*g*	*Pct.*	*Pct.*	*Pct.*	*Sec.*		*Sec.*	*cm²/sec/ m²g/cm²*	*Sec.*	*Deg*
1492	75% unbleached aspen groundwood	1	----	56.3	0.0051	11	3	2	3.6	2.3	41	44	0.053	0.135	97.0	23	2A	60	402	77	25
1494	25% bleached "Eastern" sulfite	----	1	53.9	.0052	14	4	3	4.0	2.8	39	42	.065	.147	95.4	21	5A	71	337	79	31
1493		----	3	55.0	.0053	18	8	7	5.5	3.4	35	39	.061	.166	94.9	18	9A	76	239	86	32
1498	75% unbleached aspen groundwood	1	----	55.9	.0042	11	3	2	3.6	2.6	31	34	.070	.164	94.6	56	4A	77	183	81	32
------	25% bleached aspen neutral sulfite (semichemical).	5	----	------	------	------	----	----	----	----	----	----	------	------	------	----	------	----	------	----	----
1544	75% peroxide-bleached aspen groundwood	2	----	54.4	.0042	13	7	4	9.1	6.0	28	41	.061	.153	91.0	57	6A	112	167	90	36
1545	25% bleached "Eastern" sulfite	----	1	53.1	.0039	13	10	7	9.7	7.2	34	34	.073	.146	90.5	53	10A	134	145	102	28
1546		----	3	55.4	.0042	17	16	11	11.8	8.2	35	37	.070	.187	91.0	46	10A	131	101	113	29
1523	75% unbleached aspen groundwood (slow)	14	----	52.8	.0038	13	7	8	4.0	3.1	32	32	.075	.157	97.0	109	9A	271	31	81	36
1524	25% bleached "Eastern" sulfite	----	1	55.2	.0039	15	9	13	4.5	3.6	32	32	.080	.174	97.0	97	11A	332	26	82	45
1525		----	3	55.0	.0038	18	24	26	5.7	4.1	29	30	.083	.199	97.0	85	14A	503	14	88	51
1526	100% unbleached aspen groundwood (slow)	14	3	54.7	.0037	14	1	1	5.5	3.7	21	22	.091	.202	98.0	97	13A	649	9	86	50
1537		----	----	55.4	.0040	8	2	2	2.7	2.0	58	56	.056	.116	86.0	47	2A	25	1163	68	27
1538	75% bleached aspen sulfate	7	1	55.2	.0039	15	11	11	4.8	3.6	57	57	.060	.140	85.0	51	9A	24	898	68	33
1539	25% bleached "Eastern" sulfite	----	3	54.6	.0037	22	52	43	5.8	4.2	50	50	.062	.135	84.0	56	13A	26	724	62	51
[2] 1572		----	----	56.8	.0039	15	7	6	4.8	3.3	57	58	.061	.152	86.0	66	6A	31	419	63	39
1557		----	----	55.5	.0037	9	3	3	3.3	2.1	51	61	.058	.116	86.0	84	2A	22	900	41	27
1558	75% bleached aspen soda	15	1	56.5	.0037	19	20	14	5.4	3.7	60	60	.048	.126	87.0	75	10A	24	719	57	25
1559	25% bleached "Eastern" sulfite	----	3	55.0	.0034	22	42	30	6.3	4.4	51	48	.051	.143	85.0	89	11A	27	584	57	27
[2] 1573		----	----	54.7	.0038	14	8	5	4.9	3.2	47	54	.050	.148	86.0	66	5A	30	422	63	37

See footnotes at end of table.

TABLE 1. *Comparative data on offset papers made from hardwood fibers bonded with melamine-formaldehyde resin*—Continued

Run No.	Pulp	Forest Products item No.	Melamine-formaldehyde resin added	Weight [1] 25 by 40 in., 500 sheets	Thickness	Bursting strength	Folding endurance (double folds) MIT (tension 1 kg): Machine direction	Folding endurance (double folds) MIT (tension 1 kg): Cross direction	Tensile strength: Machine direction	Tensile strength: Cross direction	Tearing resistance: Machine direction	Tearing resistance: Cross direction	Expansivity (15% change in relative humidity): Machine direction	Expansivity (15% change in relative humidity): Cross direction	Opacity (contrast ratio)	Smoothness (Bekk)	Surface pick (wax No.)	Oil penetration	Air permeability	Sizing value (dry indicator)	Curl
			Pct.	*lb.*	*Inch*	*Pts.*			*kg*	*kg*	*g*	*g*	*Pct.*	*Pct.*	*Pct.*	*Sec.*		*Sec.*	*cm³/sec/m²g/cm²*	*Sec.*	*Deg*
1541	75% bleached aspen sulfite	16	----	56.6	.0036	14	9	6	11.2	6.9	50	51	.055	.151	86.0	73	5A	67	198	102	40
1542	25% bleached "Eastern" sulfite	----	1	56.4	.0036	20	27	13	14.6	9.1	44	48	.057	.159	85.0	69	11A	72	149	104	44
1543		----	3	56.3	.0034	23	44	31	16.9	10.9	43	42	.056	.154	84.0	68	15A	79	130	126	43
1495	75% bleached aspen neutral sulfite (semichemical)	5	----	56.3	.0038	23	84	42	7.5	4.3	53	56	.086	.282	79.1	27	12A	81	114	69	120
	25% bleached strong soda																				
1496	50% bleached aspen neutral sulfite (semichemical)	5	----	56.0	.0037	20	26	16	6.3	4.0	48	53	.078	.219	83.8	55	10A	56	189	73	70
	50% bleached strong soda																				
1497	25% bleached aspen neutral sulfite (semichemical)	5	----	56.1	.0039	14	8	6	4.6	3.2	45	52	.071	.184	88.0	58	5A	31	364	67	50
	75% bleached strong soda																				
1499	67% bl. aspen, 33% bl. spruce sulfate	3	----	56.4	.0039	20	32	13	6.5	3.4	73	78	.053	.173	85.2	53	6A	37	405	73	41
1500		----	1	56.3	.0037	29	97	54	7.6	4.6	60	64	.066	.164	85.9	48	10A	40	318	78	44
1501	40% bl. aspen, 20% bl. spruce sulfate	3	----	55.0	.0040	16	11	7	5.1	3.1	58	63	.057	.135	88.2	61	5A	32	434	77	37
1502	40% bl. strong soda	----	1	55.5	.0040	24	46	17	6.9	4.4	53	59	.058	.146	87.0	63	9A	36	373	77	42
1503	75% bl. black gum (tupelo) sulfate	6	----	54.4	.0042	11	4	3	3.0	2.1	66	75	.071	.160	83.0	36	3A	15	1675	50	35
1516	25% bl. "Eastern" sulfite	----	1	55.2	.0037	19	27	23	5.0	3.5	71	75	.070	.146	84.0	92	13A	28	834	58	45
1517		----	3	53.1	.0038	24	57	49	5.6	4.1	71	65	.073	.181	83.0	50	16A	26	975	60	49
1518	100% bl. black gum (tupelo) sulfate	6	3	54.2	.0039	24	57	50	5.6	4.1	69	71	.079	.175	82.0	40	16A	20	1537	55	46
1519	75% peroxide-bl. paper birch groundwood	8	----	52.8	.0039	9	2	2	1.4	1.1	30	32	.061	.141	94.0	88	2A	79	150	54	31
1520	25% bl. "Eastern" sulfite	----	1	52.6	.0038	11	3	3	3.9	2.6	27	29	.064	.162	93.0	113	6A	87	131	25	31
1521		----	3	52.3	.0037	14	4	4	4.5	2.9	24	28	.063	.181	93.0	113	10A	123	77	33	37
1533	75% bl. paper birch sulfite	10	----	54.2	.0036	9	4	2	3.0	1.8	64	70	.052	.137	84.0	68	2A	25	1638	66	33
1534	25% bl. "Eastern" sulfite	----	1	54.6	.0036	16	16	9	4.3	2.7	67	68	.049	.140	83.0	54	10A	20	1359	73	33
1535		----	3	52.4	.0034	21	79	35	5.6	3.6	54	55	.056	.169	80.0	53	12A	20	1178	72	48
1508	75% bl. paper-birch neutral sulfite (semichemical)	9	----	53.1	.0034	38	382	169	9.6	5.6	51	59	.098	.303	76.0	47	18A	224	43	57	144
	25% bl. strong soda																				
1509	50% bl. paper-birch neutral sulfite (semichemical)	9	----	54.6	.0035	28	103	41	7.7	4.7	48	54	.091	.252	83.0	66	13A	99	112	59	92
	50% bl. strong soda																				
1510	25 bl. paper-birch neutral sulfite (semichemical)	9	----	55.7	.0037	20	19	13	6.1	3.9	48	53	.082	.195	88.0	115	10A	59	235	56	58
	75% bl. strong soda																				
1568		----	----	53.3	.0037	9	3	2	2.7	1.8	53	53	.059	.133	88.0	66	2A	16	1397	51	38
1569	75% bl. beech sulfate	12	1	54.9	.0039	13	4	6	3.4	2.4	52	50	.050	.133	89.0	47	6A	15	1227	60	35
1570	25% bl. "Eastern" sulfite	----	3	52.9	.0040	17	10	10	4.7	3.6	50	47	.055	.150	88.0	45	11A	17	1102	57	36
[2] 1571		----	----	53.1	.0039	14	6	6	4.4	3.0	46	44	.060	.174	86.0	52	10A	27	565	55	42
1529	75% bl. Douglas fir neutral sulfite (semichemical)	13	----	52.9	.0036	21	163	53	5.5	3.4	112	128	.061	.165	79.0	66	11A	62	302	50	48
	25% bl. strong soda																				
1530	50% bl. Douglas fir neutral sulfite (semichemical)	13	----	54.1	.0035	19	79	28	5.1	3.2	98	112	.061	.164	85.0	62	10A	61	326	56	47
	50% bl. strong soda																				
1531	25% bl. Douglas fir neutral sulfite (semichemical)	13	----	54.0	.0036	15	14	9	4.2	2.8	79	87	.048	.133	88.0	70	7A	52	425	61	36
	75% bl. strong soda																				
1562	75% bl. strong soda	----	----	53.2	.0034	9	4	4	3.3	2.5	47	49	.049	.123	91.0	148	3A	36	416	53	32
1563	25% bl. "Eastern" sulfite	----	1	54.0	.0033	16	10	8	4.8	3.5	46	47	.056	.132	90.0	147	7A	36	359	69	33
1564		----	3	54.3	.0033	19	18	16	5.4	4.0	46	44	.054	.136	89.0	151	11A	38	327	67	36
1540	50% bl. strong soda	----	----	54.8	.0040	12	6	4	3.7	2.6	61	63	.049	.126	88.0	64	3A	34	556	93	31
1560	50% bl. "Eastern" sulfite	----	1	54.4	.0036	17	15	12	4.7	3.3	57	58	.056	.142	87.0	79	10A	28	309	45	36
1561		----	3	53.6	.0031	20	29	21	5.9	3.8	46	44	.058	.146	87.0	166	13A	41	295	69	43

[1] All physical tests made under conditions of 50-percent relative humidity and 73° F, by the standard methods of the Technical Association of the Pulp and Paper Industry, except Carson air permeability.

[2] Stock was given more drastic beating in an attempt to obtain greater strength without the use of a bonding resin.

TABLE 2. *Effect of melamine resin on tensile breaking strength of papers* [1] *containing aspen pulp produced by various pulping processes*

Amount of melamine	Groundwood process		Sulfate process		Sulfite process		Soda process	
	Machine direction	Cross direction	Machine direction	Cross direction	Machine direction	Cross direction	Machine direction	Cross direction
Percent	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*
	9.1	6.0	2.7	2.0	11.2	6.9	3.3	2.1
1	9.7	7.2	4.8	3.6	14.6	9.1	5.4	3.7
3	11.8	8.2	5.8	4.2	16.9	10.9	6.3	4.4

[1] 75% aspen (hardwood) pulp, 25% sulfite softwood pulp.

TABLE 3. *Effect of melamine resin on tensile breaking strength of papers* [1] *containing hardwood pulps produced from various species of wood by the sulfate pulping process*

Amount of melamine	Aspen		Black gum		Beech	
	Machine direction	Cross direction	Machine direction	Cross direction	Machine direction	Cross direction
Percent	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*	*kg/15 mm*
	2.7	2.0	3.0	2.1	2.7	1.8
1	4.8	3.6	5.0	3.5	3.4	2.4
3	5.8	4.2	5.6	4.1	4.7	3.6

[1] 75% hardwood pulp, 25% sulfite softwood pulp.

expansivity of the sheet was nearly as much as when 3 percent of bonding resin was used (run 1493) and the air permeability less. The aspen neutral sulfite pulp was not a good substitute for the resin bonding in developing desirable properties in the finished paper (fig. 3).

Peroxide-bleached aspen groundwood, slow (item 2).—The papers of runs 1544–6 showed improvement in strength properties as a result of bleaching the pulp, but the expansivity was somewhat high when the percentage of bonding resin was increased. Except for improvement in color, whether the effect on other qualities would warrant the extra cost of the bleaching operations is doubtful (fig. 4).

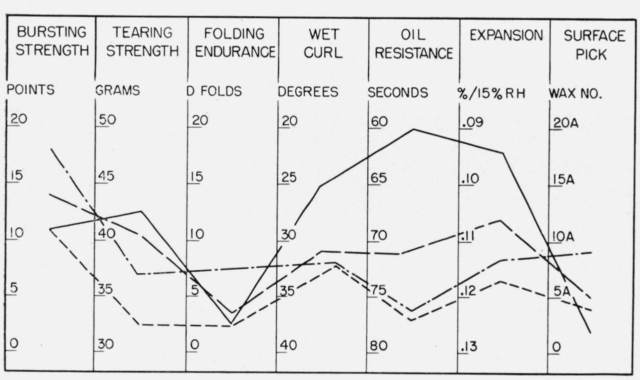

FIGURE 3. *Effect of melamine resin in papers containing unbleached aspen groundwood pulp (FPL item 1).*

——— 1492, blank, 75% unbleached aspen groundwood, 25% bleached eastern sulfite; —— —— 1494, 1% M, 75% unbleached aspen groundwood, 25% bleached eastern sulfite; ——·—— 1493, 3% M, 75% unbleached aspen groundwood, 25% bleached eastern sulfite; - - - - 1498, blank, 75% unbleached aspen groundwood, 25% aspen neutral sulfite.

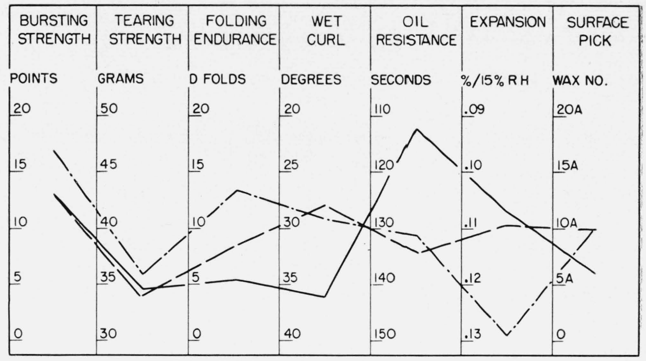

FIGURE 4. *Effect of melamine resin in papers containing peroxide-bleached aspen groundwood pulp (FPL item 2).*

——— 1544, blank, 75% peroxide-bleached aspen groundwood, 25% eastern sulfite; —— —— 1545, 1% M, 75% peroxide-bleached aspen groundwood, 25% eastern sulfite; ——·— 1546, 3% M, 75% peroxide-bleached aspen groundwood, 25% eastern sulfite.

Unbleached aspen book-grade groundwood pulp, slow (item 14).—The strength properties of papers made of this pulp (runs 1523–6) were better in general than for the papers made from the free unbleached aspen groundwood (item 1), but the expansivity was too high and the air permeability of the sheet very low. The folding endurance for paper (run 1526) made from 100-percent book-grade groundwood pulp and 3 percent of bonding resin was almost negligible.

Aspen sulfate pulp (item 7).—Papers (runs 1537–9) with good strength and resistance to surface pick, combined with low expansion, were made from a mixture of this pulp with only 25 percent of sulfite pulp (coniferous) and having 1 and 3 percent, respectively, of melamine-formaldehyde resin added for bonding (fig. 5).

Run 1572 was made to try to develop strength in the paper as a result of beating instead of with melamine resin. The beating did not develop sufficient strength however, whereas bonding with 3 percent of melamine-formaldehyde resin produced

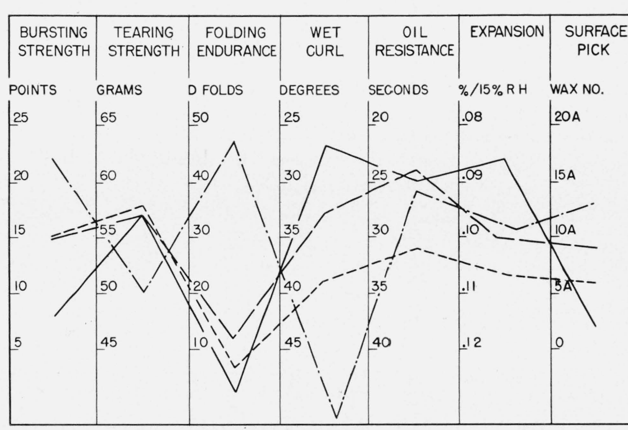

FIGURE 5. *Effect of melamine resin in papers containing aspen sulfate pulp (FPL item 7).*

——— 1537, blank, 75% bleached aspen sulfate; 25% eastern sulfite; —— —— 1538, 1% M, 75% bleached aspen sulfate, 25% eastern sulfite; ——·—— 1539, 3% M, 75% bleached aspen sulfite, 25% eastern sulfate; - - - - 1572, blank, 75% bleached aspen sulfate, 25% eastern sulfite, long beating time.

good strength properties without appreciable beating. The more drastic beating increased the expansivity above that produced by the bonding resin (fig. 5).

Aspen soda pulp (item 15).—Generally satisfactory papers (runs 1557–9) were obtained with this pulp when either 1 or 3 percent of bonding resin was used. Drastic beating (run 1573) did not develop the necessary strength in the paper to the extent that 3 percent of melamine-formaldehyde resin did, and it increased expansivity and greatly reduced air permeability (fig. 6).

Aspen sulfite pulp (item 16).—This is another pulp from which papers (runs 1541–3) with good strength and resistance to surface pick, combined with low expansivity, were produced when bonding resin was used (fig. 7).

Aspen neutral sulfite pulp (item 5).—Papers (runs 1495–7) made from this pulp mixed with varying percentages—25, 50, and 75, respectively—

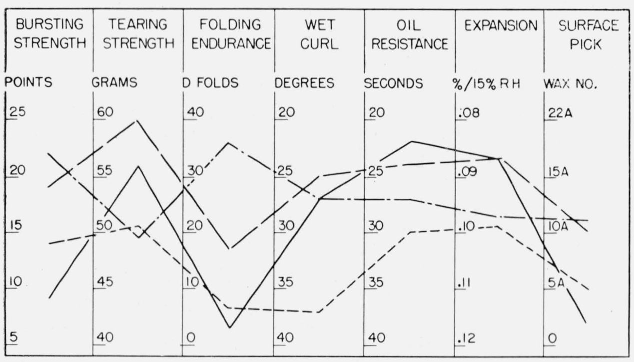

FIGURE 6. *Effect of melamine resin in papers containing aspen soda pulp (FPL item 15).*

——— 1557, blank, 75% bleached aspen soda, 25% bleached eastern sulfite; ——— ——— 1558, 1 M, 75% bleached aspen soda, 25% bleached eastern sulfite; ——. —— 1559, 3M, 75% bleached aspen soda, 25% bleached eastern sulfite; - - - - 1573, blank, longer beating time.

of soda pulp (hardwood), with no bonding resin added, were unsatisfactory because of very high expansivity and curl.

Mixed aspen and spruce sulfate pulp (item 3).—The papers (runs 1499 and 1500) from 100-percent sulfate pulp (67 percent of aspen and 33 percent of spruce), without and with 1 percent of bonding resin, had satisfactory strength properties but with expansivity nearing the border line (fig. 8).

In order to get a softer sheet with the bleached sulfate, and less expansivity, it was decided to make two more runs (1501–2) duplicating runs 1499 and 1500 except in the pulp furnish, which included a strong hardwood soda pulp. The pulp furnish for the runs (1501–2) was 40 percent of sulfate, aspen; 20 percent of sulfate, spruce; and 40 percent of soda, hardwood. The strength properties of the papers were fairly good and the expansivity satisfactory, but the resistance to surface picking was somewhat less. However, it is believed that aspen sulfate pulp prepared alone and then mixed with coniferous sulfite in 75- to 25-percent proportion respectively, and having 3 percent of melamine-formaldehyde resin

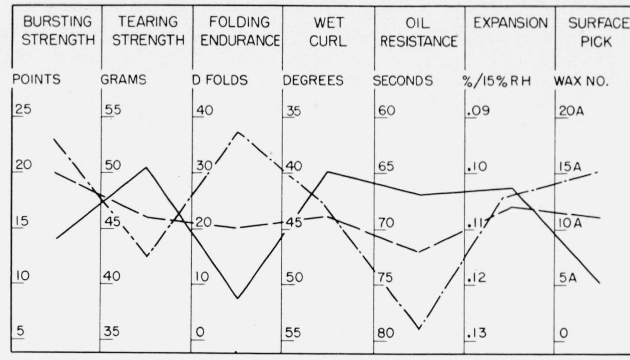

FIGURE 7. *Effect of melamine resin in papers containing aspen sulfite pulp (FPL item 16).*

——— 1541, blank, 75% bleached aspen sulfite, 25% bleached eastern sulfite; —— —— 1542, 1% M, 75% bleached aspen sulfite, 25% bleached eastern sulfite; ——. —— 1543, 3% M, 75% bleached aspen sulfite, 25% bleached eastern sulfite.

added, would give paper equally as good, if not better, for offset printing (fig. 8).

Black gum (tupelo) sulfate pulp (item 6).—When this pulp was used in combination with 25 percent of sulfite (coniferous) and had 1 or 3 percent of bonding resin added, the papers made (runs 1503–16–17) were of good strength and had very high resistance to surface pick, but the expansivity was too high. The expansivity of paper from run 1518, 100 percent of black gum sulfate pulp with 3 percent of bonding resin, was also too high (fig. 9).

Since black gum sulfate pulp looks so promising in strength development and resistance to surface pick, it seems likely that if the pulp were combined with another hardwood pulp, instead of a coniferous, a very satisfactory paper could be obtained if 1 to 3 percent of bonding resin were used.

Peroxide-bleached paper-birch groundwood (item 8).—On the whole, in these papers (runs 1519–21) the melamine resin had little beneficial effect.

Paper-birch sulfite pulp (item 10).—Papers (runs 1533–5) with good strength and resistance to surface pick, combined with low expansion, were made from this pulp in combination with only 25 percent of sul-

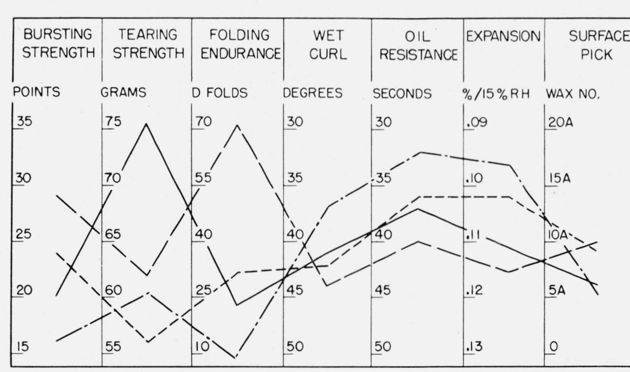

FIGURE 8. *Effect of melamine resin in papers containing aspen and spruce sulfate pulp (FPL item 3).*

——— 1499, blank, 100% bleached sulfate, 67% aspen, 33% spruce; —— —— 1500, 1% M, 100% bleached sulfate, 67% aspen, 33% spruce; ——. —— 1501, blank, 60% bleached sulfate (67% aspen, 33% spruce), 40% strong soda; - - - - 1502, 1% M, 60% bleached sulfate (67% aspen, 33% spruce), 40% strong soda.

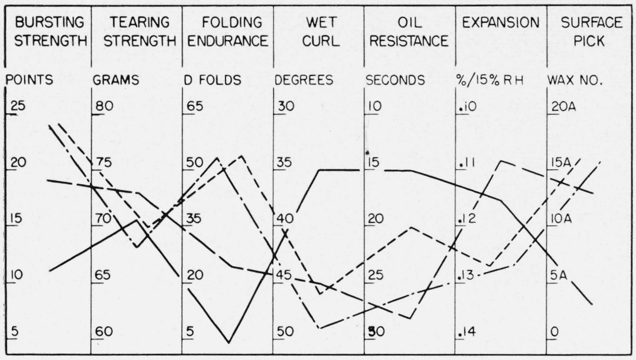

FIGURE 9. *Effect of melamine resin in papers containing black gum sulfate pulp.(FPL item 6).*

——— 1503, blank, 75% bleached black gum (tupelo) sulfate, 25% eastern sulfite; ——— ——— 1516, 1% M, 75% bleached black gum (tupelo) sulfate, 25% eastern sulfite; ——.—— 1517, 3% M, 75% bleached black gum (tupelo) sulfate, 25% eastern sulfite; - - - - 1518, 3% M, 100% bleached black gum (tupelo) sulfate.

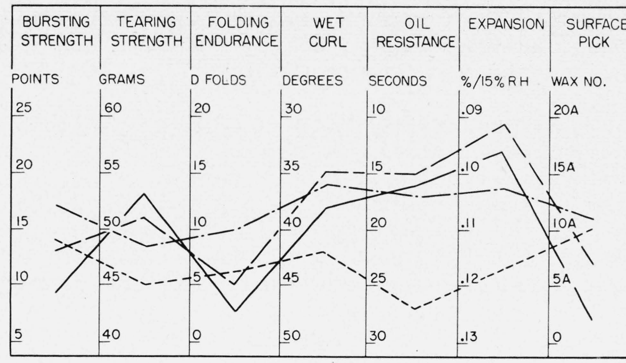

FIGURE 11. *Effect of melamine resin in papers containing beech sulfate pulp (FPL item 12).*

——— 1568, blank, 75% bleached beech sulfate, 25% bleached eastern sulfite; ——— ——— 1569, 1% M, 75% bleached beech sulfate, 25% bleached eastern sulfite; ——.—— 1570, 3% M, 75% bleached beech sulfate, 25% bleached eastern sulfite; - - - - 1571, blank, longer beating time.

fite pulp (coniferous) and having 1 or 3 percent of bonding resin added (fig. 10).

Paper-birch neutral sulfite pulp (item 9).—As shown in the table the papers (runs 1508–10) made from this pulp and varying percentages—25, 50, and 75, respectively—of soda pulp (hardwood) without bonding resin added were unsatisfactory because of very high expansivity and curl.

Beech sulfate pulp (item 12).—Beech sulfate was another pulp from which papers (runs 1568–70) were produced with satisfactory strength and resistance to surface pick, combined with low expansivity when 1 or 3 percent of melamine-formaldehyde resin was added. Drastic beating alone did not develop the necessary strength in the paper (run 1571). Moreover, it increased the expansivity above that of the paper in which bonding resin was used and reduced tearing strength and air permeability (fig. 11.)

Douglas-fir neutral sulfite pulp (item 13).—This is a coniferous wood pulp, whereas the other pulps supplied by Forest Products Laboratory were wholly or predominately hardwood. The papers (1529–31) made from the Douglas-fir pulp mixed with soda pulp (hardwood)—25, 50, and 75 percent, respectively—without bonding resin, were fairly satisfactory, but the expansivity was approximately the maximum allowable.

Since a long-fibered pulp characterized by high strength, especially tearing resistance, was produced from Douglas fir by the neutral sulfite, semichemical process, it seems that the wood might better be cooked by one of the other pulping processes. It would thereby make available long-fibered, softer pulp, which would doubtless be satisfactory for use with such hardwood pulps as have been used in these experiments, and release the spruce sulfite pulp (coniferous) for other types of papers. Douglas fir appears to show great promise as a wood for paper-making.

Other hardwood-coniferous pulp mixtures.—To afford comparisons, two series of papers were made from a furnish of commercial bleached soda pulp (hardwood) and commercial sulfite pulp (coniferous), without and with melamine resin. For one series (runs 1562–4) 75 percent and 25 percent of the pulps, respectively, were used (fig. 12); for the other series (1540–60–61) 50 percent of each was used (fig. 13).

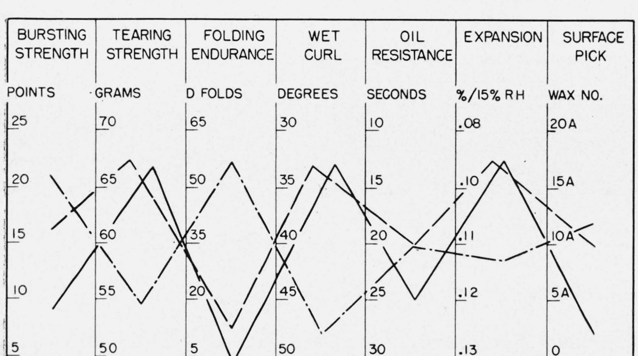

FIGURE 10. *Effect of melamine resin in papers containing paper-birch sulfite pulp (FPL item 10).*

——— 1533, blank, 75% bleached paper-birch sulfite, 25% bleached eastern sulfite; ——— ——— 1534, 1% M, 75% bleached paper-birch sulfite, 25% bleached eastern sulfite; ——.—— 1535, 3% M, 75% bleached paper-birch sulfite, 25% bleached eastern sulfite.

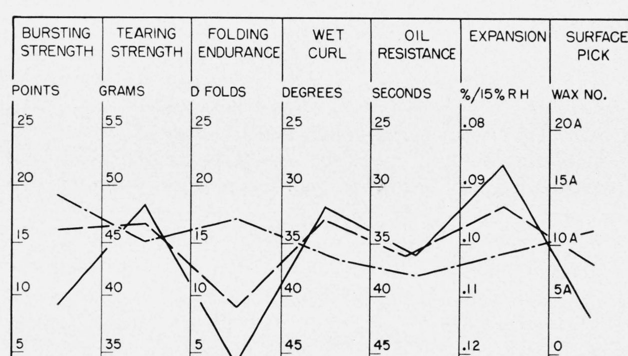

FIGURE 12. *Effect of melamine resin in papers containing Douglas-fir neutral sulfite pulp (FPL item 13).*

——— 1562, blank, 75% strong soda, 25% eastern sulfite; ——— ——— 1563, 1% M, 75% strong soda, 25% eastern sulfite; ——.—— 1564, 3% M, 75% strong soda, 25% eastern sulfite.

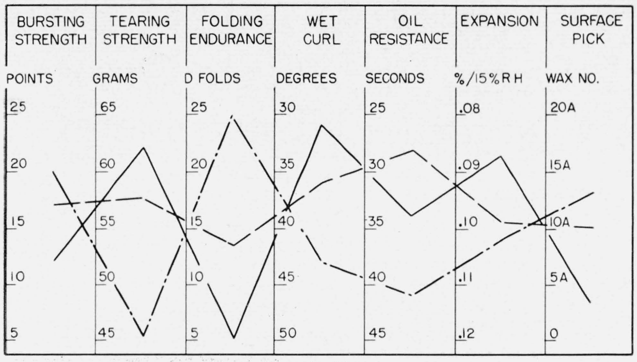

FIGURE 13. *Effect of melamine resin in papers containing commercial hardwood soda pulp and coniferous sulfite pulp.*

——— 1540, blank, 50% bleached strong soda, 50% bleached eastern sulfite;
— — — 1560, 1% M, 50% bleached strong soda, 50% bleached eastern sulfite;
—.— 1561, 3% M, 50% bleached strong soda, 50% bleached eastern sulfite.

VII. Summary

Promising results were obtained with the hardwood pulps alone and mixed in the production of lithographic-type papers. Papers with good strength and resistance to surface pick, combined with low expansion and curl, were made from the hardwood pulps with melamine-formaldehyde resin added for bonding. By use of the resin (1 or 3 percent, based on dry fiber) the paper could be made from a less hydrated stock, the strength being developed mainly by bonding the fibers with the resin instead of by the conventional beating. The pulps giving particularly promising results comprised aspen sulfate, aspen soda, aspen sulfite, birch sulfite, and black gum sulfate. The qualities of the papers made from these pulps are as good as, and in some respects better than, those of paper made from 50-percent commercial hardwood pulp and 50-percent commercial sulfite softwood pulp.

Although not a hardwood, Douglas fir was also included in the study to evaluate its paper-making characteristics. Only neutral sulfite (semichemical) pulp was used, but since the fibers were long and seemed to have high strength, especially tearing resistance, it is believed that if the pulp were prepared by any of the other chemical processes an excellent paper-making material could be produced.

In general, papers made from the pulps prepared from any of the woods by the neutral sulfite (semichemical) process were not entirely satisfactory. The pulps tended to hydrate too quickly and to develop considerable hardness, and the papers made from them had high expansivity and curl.

An example of the possibilities of resin bonding used to develop strength in papers made from hardwood pulps is shown by the measurements obtained on the papers made from 75-percent bleached aspen sulfate and 25-percent commercial sulfite pulp. With all other factors constant, the addition of 3-percent melamine-formaldehyde resin to this fiber increased the bursting strength from 8 to 22 points, the folding endurance from 2 to 46 double folds, and the resistance to surface pick from wax 2A to 13A, yet the expansivity remained low. These results were obtained without beating the fibers to any considerable extent.

Judged by the laboratory test data, the results appear very satisfactory. The performance of the experimental papers in the printing operations, however, will be the determining factor in their satisfactoriness for lithographic use.

Printing tests of them are being made in the experimental printing plant of the Lithographic Technical Foundation, and the results will be published by the Foundation. If they are satisfactory, the development of strength through the use of synthetic resins in offset papers may greatly increase the use of hardwood fibers.

The cooperation of George M. Hunt, Director, and G. H. Chidester, Chief, Division of Pulp and Paper, U. S. Forest Products Laboratory, in furnishing the pulps for this investigation is gratefully acknowledged. This investigation and the previous investigations dealing with offset papers were conducted with the counsel of an advisory committee of technicians of the paper-making and printing industries, under the Chairmanship of R. F. Reed, Research Consultant, Lithographic Technical Foundation. The investigation was made under the direction of Charles G. Weber, deceased.

WASHINGTON, May 18, 1950.