PROPERTIES OF LAMINATED PLASTICS MADE FROM LIGNIN AND LIGNIN-PHENOLIC RESIN-IMPREGNATED PAPERS

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PROPERTIES OF LAMINATED PLASTICS MADE FROM LIGNIN AND LIGNIN-PHENOLIC RESIN-IMPREGNATED PAPERS[1]

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Introduction

The Forest Products Laboratory has previously reported[2] preliminary experiments concerning the manufacture of lignin-filled laminates by the incorporation of a soda-pulp lignin into the paper-making furnish at the beater to yield paper suitable for molding into laminated plastics.

This report is concerned with the development of plastic laminates from paper impregnated with solutions of lignin or mixtures of lignin and phenolic resins. Since lignin is potentially both abundant and inexpensive, the extension of phenolic resins with lignin is attractive provided the quality of the resultant plastic is not seriously reduced. The use of all-lignin varnish impregnants for paper would not be so economical, however, as adding lignin to the beater, since this method eliminates costly items, such as refinement of lignin, the use of volatile solvents, and separate impregnation operations. The strength properties of all-lignin resin paper plastics made by either method are approximately the same, and are somewhat below those usually attained with all-phenolic resin. The use of resin varnishes made from mixtures of soda-pulp lignin and water-soluble phenolic resin in equal proportions, however, has occasionally yielded strength values approximately equal to those obtained by the use of either all water-soluble or all spirit-soluble phenolic resin. A balance of properties, particularly between water absorption and impact resistance, can be achieved by varying the proportion of lignin resin to phenolic resin or by the choice of solvent.

The work reported herein is limited and is to be considered only as a preliminary survey to determine approximately the effect of certain major variables on the properties of lignin resin and lignin-phenolic-resin paper-base laminates.

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[1] This mimeograph is one of a series of progress reports prepared by the Forest Products Laboratory to further the Nation's war effort. Results here reported are preliminary and may be revised as additional data become available.

[2] Forest Products Laboratory Restricted Mimeographs Nos. 1576, 1577, and 1579.

Materials, Processes and Methods

Resins and Solvents

The lignin resins used in this work were derived from soda-pulp process spent liquors, either by the Howard Smith Paper Mills (HSPM) or by the Mead Corporation (Meadol), or from waste sulfite liquor processed by the Marathon Chemical Company (VDP). Except as otherwise noted, the soda-process type of lignin is indicated when the term lignin is used unqualified. The phenolic resins used were of the phenol-formaldehyde thermosetting type and are identified in the tables.

Resin solutions suitable for impregnating paper must have a viscosity and solids concentration such that the required amount of resin can be introduced into the laminating paper within the limits of control of the impregnating machine. Impregnants should also penetrate the sheet rapidly, and the solvent must not be so volatile that it evaporates before penetration is complete. It should, however, be volatile enough to insure its removal in the drying tunnel.

In order to accommodate the wide range of resin content values and lignin-phenolic resin ratios desired in the laminates prepared in this study, it was necessary to use a considerable variety of solvent mixtures and Concentrations. Preliminary tests indicated roughly the range of viscosities and Concentrations that could be used to secure any desired resin content in the impregnated paper. A variety of solvent mixtures was tried in order to determine their suitability for the various lignin-phenolic resin mixtures. In general, the choice of solvents was based on the rate of penetration Of Solutions into a standard kraft paper. For lignin and for mixtures of lignin with water-soluble phenolic resin, an alcohol-acetone solvent was satisfactory, but when spirit-soluble phenolic resin 'was used, it was necessary to add Cellosolve, although this retarded the subsequent removal of the solvent in the drying tower. The addition of water, up to 35 percent, to the alcohol-acetone-Cellosolve solvent lowered the viscosity and improved the penetration Of the solutions. It also decreased the cost of the solvent.

Base Paper

Panels referred to in table 1 were laminated from one of a group Of base papers (MR-2235, -2236, -2316) made on the Laboratory's experimental paper machine from commercial black spruce sulfate pulp. The laminates referred to in table 2 were made from a high-strength base paper (MR-2424) using a special experimental black spruce sulfate pulp made at the Laboratory.

Impregnation and Laminating

The base paper was resin-treated on the impregnating machine pictured in figure 1. Tho method or rate of resin application, speed of travel of the paper, air velocity and air temperature in the drying tunnel were changed as required to obtain the desired final resin and volatile contents. Resin content was determined by the difference in weight between an area of the air-dry paper and an equal area of the paper immediately after it emerged from the impregnator drying tunnel, expressed as a percentage of the treated-paper weight. Volatile content as used in this report refers to the difference in weight between a resin-treated sheet immediately after it emerged from the impregnator drying tunnel and its weight after drying in an oven at 160° C. for 10 minutes, tho weight difference being expressed in percent of the first weight .

In general, an early-condensed, (water-soluble) type of phenolic resin shoved advantages over a more advanced (spirit-soluble) resin for solutions incorporating lignin. Not only were better plastic properties obtained, but the difficulties of preparing solutions and of obtaining penetration during impregnations were minimized by the use of this type resin. Due to the wide variations in viscosity and other characteristics of the solutions it was frequently necessary to alter the solvents, change concentrations, and vary the techniques of impregnation to obtain the desired conditions. Some of these changes, made to overcome practical operating difficulties, may have partially obscured the effects of other variables. For example, the use of Cellosolve, to reduce the evaporative losses of the solvent and thereby permit more thorough penetration of the resin, showed evidence of being detrimental to tho bonding of the laminates if it was not almost completely removed in drying the sheet. Also, a loss in impact strength is known to accompany the use of water as a constituent of the resin solvent.

The panels whose properties are recorded in table 1 were parallel-laminated, and those in table 2 were cross-laminated. All panels were cooled der pressure in the laminating press. Two preliminary series were run to determine suitable cure conditions as well as to determine the maximum extension of phenolic resin which would permit the panel to be hot drawn from the press.

Testing

Toughness was determined on the Forest Products Laboratory intermediate capacity toughness machine using an unnotched specimen 7/16 inch wide by 3-1/2 inches long, tested on a span of 2-1/2 inches. The total energy required to break the specimen was divided by the specimen width and corrected by proportion to 0.125 inch thickness to obtain the values recorded in table 1. All other properties were obtained according to procedures set forth in "Proposed Federal Specification for Organic Plastics; General Specification (Methods of Physical Tests)" July 7, 1942 or superseding specifications.

Discussion of Results

Data showing the effect of resin content (all lignin) (series 1), lignin-phenolic resin ratio (series 2), type of lignin (series 3), and laminating pressure (series 4) on the properties of the laminates using paper made from commercial sulfate pulp are given in table 1. Table 2 presents a comparison of properties obtained in the plastics when aqueous and non-aqueous solvents were used in impregnating a special Forest Products Laboratory experimental paper with Meadol lignin and phenolic-resin mixtures.

The effects of resin content (all lignin) of the plastic, as shown in series 1, were determined to aid in the choice of limits of the amount to be used in the subsequent study of lignin-phenolic ratios. A loss of about 15 percent in ultimate tensile strength and about 9 percent in tensile modulus of elasticity was observed as the resin content was increased from 25 to 40 percent. The water absorption was decreasad from 13.6 to 7.5 percent within the same range. Some delamination was observed when 25 percent resin was used, but the flow and bonding were improved at higher values. The strength properties obtained at 36 percent resin content were approximately equal to those usually obtained from the all lignin-filled laminates referred to previously.

The data in series 2 indicate that the water-soluble phenolic resin can be extended to a mixture containing about 60 percent lignin with no appreciable change in the resultant properties. Beyond this extension there was a general impairment of all properties except toughness, which was increased. Extending the resin mixture from 60 percent to 90 percent lignin caused a decrease in the maximum compressive strength of about 33 percent, and in the maximum tensile strength, about 12 percent over the same range. When 33 percent lignin was used the water absorption was 1.5 percent; at 71 percent lignin it had increased to only 1.8 percent, but at 100 percent lignin it had increased to 9.6 percent, showing that the water resistance was greatly impaired as an all-lignin resin was approached. The toughness followed a similar pattern; that is, it was substantially constant up to about 70 percent. lignin and then increased rapidly upon further extension of the phenolic resin. Over the range of extension of 50 to 100 percent lignin in the resin mixture, the toughness increased from 14.3 to 48.9 inch-pounds per inch of width. The specific gravity of the panel made with all water-soluble phenolic resin was only 1.33, showing that under the conditions used, 500 pounds per square inch laminating pressure was insufficient to completely densify the paper which has been swollen by the water solvent.[3] Tho high volatile content of plastic No. 2235-22 was probably due to residual Cellosolve in the plastic that may have been detrimental to the bonding as previously indicated.

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[3] Subsequent to this research, it has been shown by British investigators that paper impregnated with a water-soluble resin can be laminated at lower pressures if it has been calendered after impregnation and drying, or if the base paper has been pretreated with a small amount of resin, calendered, and then cured before the main impregnation.

When spirit-soluble phenolic resin was extended with lignin over the same range of percentages, the properties were, in general, slightly inferior to those obtained with the water-soluble type resin, and, as the lignin content was increased, the strength properties were reduced, except toughness which passed through a minimum because of an abnormal initial value. It is known that a loss in impact strength accompanies the use of water in the phenolic-resin solvent and it was to this effect that the minimum was attributed. When the phenolic resin was extended up to 80 percent lignin the water absorption was increased from 1.8 to 6.6 percent. Better water resistance for an equal amount of phenolic resin was obtained by using the water-soluble phenolic resin. When a spirit-soluble phenolic resin was used, the ultimate tensile strength was decreased from 31,840 pounds per square inch with 100 percent phenolic to 23,880 pounds per square inch with 20 percent phenolic resin, and the modulus of elasticity in tension was decreased from 2,636,000 to 2,281,000 pounds per square inch over the same range. Extending the spirit-soluble phenolic resin to 60 percent lignin reduced the maximum edgewise compressive strength by about 40 percent and lowered the modulus of elasticity in compression by about 9 percent.

A series of panels was made to determine the limiting lignin-phenolic resin ratio which would permit hot drawing from the press without blistering. The series showed that water-soluble phenolic resin could be extended up to about 60 percent lignin, and that with spirit-soluble phenolic resin the approximate limiting amount, was about 50 percent. Some tendency to delaminate was observed in the panels made with highly extended spirit-soluble phenolic resin. It was not determined to what extent this may have been caused by the use of Cellosolve in the solvent.

A limited amount of work was done to compare three different commercial lignins. The data obtained on only three panels, each made with a resin containing 50 percent of a different lignin are given in series 3. Variations in the results may be due to the different solvents used, to the limitations of the data, to differences in the commercial lignins, or to a combination of these factors.

As shown in series 4, when mixtures of lignin and water-soluble phenolic resin in equal proportions were used, the effect of increasing laminating pressure in the range of 250 to 500 pounds per square inch was to reduce the toughness slightly, although the change in other properties was not appreciable. This was also true for a 90 to 10 proportion of lignin to water-soluble phenolic resin although the water absorption was decreased from 6.2 to 4.1 as tho pressure was increased from 250 to 500 pounds per square inch. When a 90 percent lignin-10 percent spirit-soluble phenolic resin mixture was used, the ultimate tensile strength was increased. from 20,920 to 23,770 pounds per square inch, the maximum compressive strength from 11,450 to 13,380 pounds per square inch, and the modulus of elasticity in tension from 2,196,000 to 2,431,000 pounds per square inch as the laminating pressure was increased from 250 to 500 pounds per square inch.

A laminating pressure of 250 pounds per square inch was not sufficient to compress the paper containing pure lignin beyond a specific gravity of about 1.22 in the plastic, resulting in poor bonding and also a high water absorption. The use of 500 pounds per square inch pressure was required to produce a laminate with a specific gravity of 1.36.

The importance of the effect of resin solvent is shown in table 2, representing the use of both aqueous and non–aqueous solvents for each of two lignin and water–soluble phenolic rosin ratios. In the 50 to 50 resin proportion the increased resin penetration into the paper due to the swelling action of the aqueous solvent probably accounts for the lowered water absorption from 2.2 to 0.9 percent. The maximum compressive strength was increased from 24,640 to 27,240 pounds per square inch, but the flatwise Izod impact strength was reduced from 4.28 to 1.93 foot–pounds per inch of notch. The same trends were found when the 75 to 25 lignin to phenolic–resin ratio was used, although all properties excepting impact strength were reduced because of the greater extension of the phenolic resin.

The dimensional change in thickness upon 24–hour water immersion when using a 50 to 50 lignin to water–soluble phenolic–resin mixture was only 0.64 percent as compared with 1.1 percent when pure water-soluble phenolic resin was used, and 2.18 percent when pure spirit-soluble phenolic resis was used. not determined why the water absorption was so low and the dimensional stability was so high. Further work must be done to establish this effect more fully.

A comparison of panels made with pure phenolic resin, and the extended phenolic–resin materials of table 2, showed that by changing the amount of lignin or choosing an aqueous or nonaqueous solvent the resultant properties could be varied over a wide range, especially the properties of impact resistance, dimensional stability, and water absorption.

The properties of plastic made with a 50 percent lignin and 50 percent water–soluble phenolic resin diluted with a nonaqueous solvent (No. 2424-6) were approximately equal to those obtained with pure spirit–soluble resin. When an aqueous solvent was used (No. 2424–7) the properties obtained approximated those encountered when pure water-soluble phenolic resin was used.

Conclusions

The following conclusions can be drawn from the data obtained on plastics made under the conditions described:

1. Water–soluble phenolic resin can be extended with as much as 60 percent soda–pulp–process lignin without appreciably altering the properties of the resultant plastic.

2. Spirit-soluble phenolic resin can be extended with soda-pulp-process lignin, but the tensile and compressive strength values decrease with an increase in the percentage of lignin. The toughness was increased as the lignin portion of the resin mixture was increased from 33 to 100 percent.

3. satisfactory laminates can be made using 250 pounds per square inch laminating pressure when phenolic resins are extended with lignin up to about 50 percent, but when higher percentages of lignin are used, laminating pressures of 500 or more poounds per square inch may be required.

4. The properties of laminates made with soda-pulp-process lignin-extended water-soluble phenolic resins can be varied over a considerable range by the use of aqueous or nonaqueous dilutents. Impact strength, water absorption, and dimensional stability are the properties affected most by the solvent.

Table 1.—Properties of laminated plastics made from lignin and lignin-phenolic resin-impregnated sulfate papers[1]

Plastic number	Resin[2]				Solvent				Impregnating conditions		Laminating conditions[3]			Properties of laminated plastic[4]							
														Tension		Compression (Edgewise)					
	Phenolic		Lignin		95 percent ethyl alcohol	Acetone	Water	Cellosolve	Resin content	Volatile content	Temperature	Pressure	Heating time	Ultimate	Modulus of elasticity	Ultimate	Yield strength at .05 percent strain offset	Modulus of elasticity	Forest Products Laboratory toughness	Specific gravity	Water absorption
	Type	Percent	Type	Percent	Percent	Percent	Percent	Percent	Percent	Percent	°F.	Lb. per sq. in.	Minutes	Lb. per sq. in.	1,000 lb. per sq. in.	Lb. per sq. in.	Lb. per sq. in.	1,000 lb. per sq. in.	In.-lb. per in. width at 0.125 inch thickness		Percent
Series 1.—Effect of resin (lignin) content																					
2235-2			H.S.P.M.	100	70	30			25	5.0	356	500	10	27,060	2,745	12,820	7,400	2,646	47.8	1.38	13.6
-3			do.	100	70	30			30	5.1	356	500	10	26,020	2,729	13,940	7,450	2,474	49.6	1.38	13.1
-4			do.	100	70	30			36	5.2	356	500	10	24,620	2,558	13,780	6,960	2,392	48.9	1.39	9.6
-5			do.	100	70	30			40	5.1	356	500	10	23,000	2,497	13,680	6,720	2,031	48.4	1.42	7.5
Series 2.—Effect of extending phenolic resins with lignin																					
2235-19	Water-soluble	100					100		35	5.0	325	500	15	28,580	2,617	21,980		2,561		1.33	2.6
-6	Do.	67	H.S.P.M.	33	75	25			35	5.2	335	500	15	29,390	2,792	22,380	9,780	2,482	15.5	1.41	1.5
-7	Do.	50	do.	50	75	25			36	5.0	335	500	15	30,020	2,851	21,750	9,220	2,374	14.3	1.41	1.5
-8	Do.	40	do.	60	75	25			35	5.1	335	500	15	27,660	2,608	21,640	8,760	2,408	17.0	1.42	1.8
-9	Do.	29	do.	71	75	25			35	5.0	335	500	30	25,650	2,384	19,810	7,480	2,151	16.0	1.42	1.8
-10	Do.	20	do.	80	75	25			35	5.3	335	500	30	23,530	2,406	18,660	7,690	2,194	23.5	1.38	2.5
-22	Do.	10	do.	90	63	25		12	36	7.5	335	500	15	24,160	2,313	14,420		2,045	32.8	1.41	7.7
-4			do.	100	70	30			36	5.2	356	500	10	24,620	2,558	13,780	6,960	2,392	48.9	1.39	9.6
2235-1	Spirit-soluble	100			100				37	4.5	325	500	12	31,840	2,636	19,880	7,400	2,240	28.5	1.41	
-11	Do.	67	H.S.P.M.	33	10	38	34	18	35	5.2	335	500	15	29,960	2,544	16,760	7,820	2,165	18.1	1.40	1.8
-12	Do.	50	do.	50	10	38	34	18	35	5.1	335	500	15	29,060	2,606	13,480	7,270	2,135	21.9	1.41	3.1
-13	Do.	40	do.	60	10	38	34	18	35	5.1	335	500	15	27,980	2,556	11,920	6,200	2,044	24.7	1.40	4.6
-14	Do.	29	do.	71	10	38	34	18	35	5.2	335	500	15	27,630	2,498	11,700	6,210	2,042	31.7	1.39	6.6
-15	Do.	20	do.	80	10	38	34	18	35	5.5	335	500	15	23,880	2,281	11,560	5,710	1,902	41.0	1.38	6.6
-4			do.	100	70	30			36	5.2	356	500	10	24,620	2,558	15,780	6,960	2,392	48.9	1.39	9.6
Series 3.—Effect of different types of lignin																					
2316-5B	Water-soluble	50	H.S.P.M.	50	62	25		13	46	4.4	335	500	15	25,050	2,329	23,250		2,040	9.1	1.40	1.0
-19	Do.	50	Meadol	50	67	25		8	42	5.5	335	500	15	27,840	2,631	22,780	11,360	2,304	13.5	1.43	1.5
-23	Do.	50	Marathon	50	67	11	14	8	42	7.4	335	500	15	27,710	2,831	20,520			15.2	1.37	3.6
Series 4.—Effect of laminating pressure																					
2316-5A	Water-soluble	50	H.S.P.M.	50	62	25		13	46	4.4	335	250	15	25,200	2,253	23,610		2,048	12.1	1.39	1.1
-5B	Do.	50	do.	50	62	25		13	46	4.4	335	500	15	25,050	2,329	23,250		2,040	9.1	1.40	1.0
2316-3A	Water-soluble	10	H.S.P.M.	90	53	41		6	47	7.6	335	250	15	19,250	1,905	11,120		1,774	39.1	1.38	6.2
-3B	Do.	10	do.	90	53	41		6	47	7.6	335	500	15	20,090	1,962	12,060		1,915	31.3	1.40	4.1
2316-11A	Spirit-soluble	10	H.S.P.M.	90	50	37		13	36	6.2	335	250	15	20,930	2,196	11,450		1,578	32.3	1.30	13.3
-11B	Do.	10	do.	90	50	37		13	36	6.2	335	500	15	22,770	2,431	13,380		1,776	33.6	1.39	12.2
2236-5A			H.S.P.M.	100	70	30			36	6.1	356	250	10	20,960	2,196	9,550		1,954	30.5	1.22	47.6
-5B			do.	100	70	30			36	6.1	356	500	10			12,130		2,096	37.3	1.36	14.2

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[1] The base paper was made on the Forest Products Laboratory experimental machine using commercial sulfate pulp. (Ship. No. 1871 for MR-2235 [illegible]. and Ship. No. 1942 for MR-2316.)

[2] The spirit-soluble phenolic resin used was Bakelite BV-16526, and the water-soluble phenolic was Bakelite BR-15100. Edward Smith Paper Mills, Ltd. lignin (ESPM) and Meadol lignin were prepared from soda-pulp-process spent liquor, while the Marathon VDP lignin was prepared from sulfite-pulp waste liquor.

[3] All panels were parallel laminated in construction and were cooled to approximate room temperature under pressure before they were removed from the press.

[4] Strength tests, with the exception of toughness, were made in accordance with "Proposed Federal Specification for Organic Plastics, General Specification (Methods of Physical Tests)," July 7, 1942. The Forest Products Laboratory toughness test method is described in the text. Tests were made in the machine direction. The properties are the average of 2 or 3 tension, 2 compression, 2 water absorption, and 5 toughness tests of each plastic.

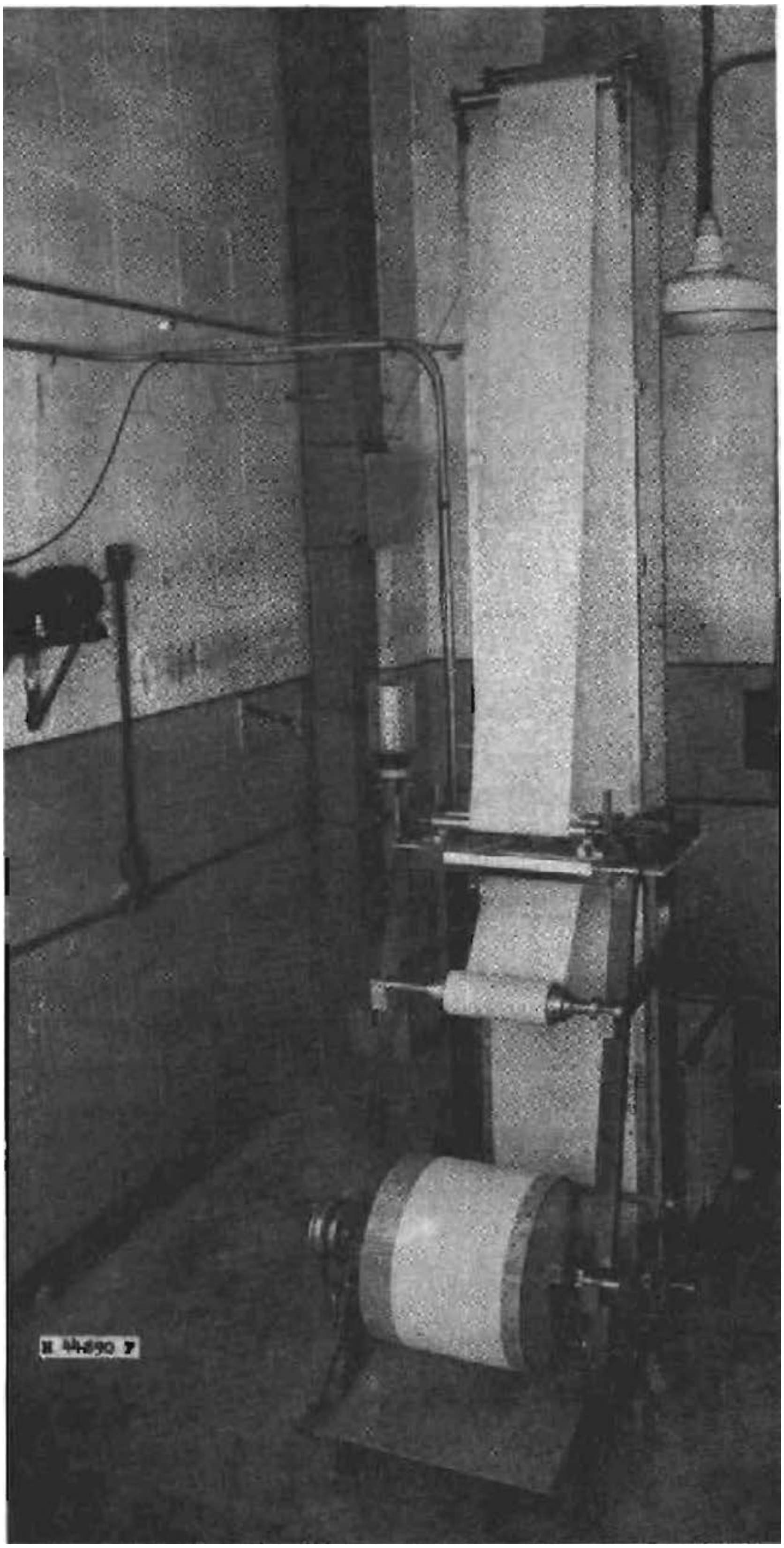

Figure 1.--The Forest Products Laboratory resin impregnator and dryer, for preparing laminating paper.

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