U.S. DEPARTMENT OF AGRICULTURE • FOREST SERVICE • FOREST PRODUCTS LABORATORY • MADISON, WIS.

In Cooperation with the University of Wisconsin

U. S. FOREST SERVICE
RESEARCH NOTE

FPL-084

DECEMBER 1964

CHEMICAL TREATMENTS FOR IMPROVING COMPRESSIVE STRENGTH OF LINERBOARD AT HIGH MOISTURE CONDITIONS

Summary

Various chemical treatments have been investigated at the Forest Products Laboratory for improving the compressive strength of linerboard exposed at high humidities and after water–soaking. Phenolic resins have been among the more promising chemicals studied, but they vary in performance. The low–condensed water–soluble phenolic resins have given some of the highest compressive strengths, but generally caused more embrittlement of the board, as noted by low tearing resistance and folding endurance. The medium–condensed phenolic resins gave only moderate increases in compressive strength but did not produce as great a loss in other desirable properties.

For maximum efficiency, most phenolic resins required heat to cure them. Resorcinol resin added to the phenolic resin mixture accelerated the cure of the phenolic resin, but the resorcinol reduced the compressive strength of the board.

Melamine resins and hydrocarbon resins also improved the compressive strength, but not as much as certain phenolic resins. No improvement was noted with the latices.

Both starch and protein treatments were highly effective at low moisture conditions, but rapidly lost their effectiveness at high moisture. The addition of a low–condensed type of water–soluble phenolic resin to a starch mixture gave a treatment that was nearly as effective at 90 percent relative humidity as the medium–condensed phenolic resins. The starch–phenolic treatments, however, were not as good after water–soaking as the phenolic–resin treatments.

CHEMICAL TREATMENTS FOR IMPROVING COMPRESSIVE STRENGTH OF LINERBOARD AT HIGH MOISTURE CONDITIONS[1]

By

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Introduction

In the packaging industry, the familiar fiber box has proven itself by carrying billions of items safely to the consumer at low cost. Under most uses the fiber container performs satisfactorily as long as it is kept at ordinary moisture conditions. However, if the container is stored or subjected to high moisture conditions, it rapidly loses its compressive strength.

In shipping or storing many items, the box itself--not the contents--has to carry the load. In the design of containers, the packaging engineer is concerned with the top-to-bottom compressive strength, or in other words, the stacking strength of the box

In the storage of perishable commodities, such as fruits and vegetables, the conditions are far from ideal for fiber containers. Some items require low-temperature storage. Commodities such as bananas require extremely high humidity for ripening. The produce itself also gives off a surprising amount of moisture during storage, thus raising the moisture content of the container. Furthermore, containers may be passed through a cooling process where water is sprayed on the container or even topped with ice during shipment.

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[1] In cooperation with the Packaging Evaluation Agency, (MOSPR), Mobile Air Material Area, Brookley Air Force Base, Mobile, Ala.

[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

Fiber containers are stored in warehouses all over the world. Usually, it is impossible to control the conditions in these warehouses. In some areas high relative humidity for long periods of time results in loss of stacking strength and the boxes topple. This problem has plagued the military agency, as well as the domestic shipper.

In 1959, at the request of the Air Force .Packaging Laboratory, Brookley Air Force Base, Ala., a project was started at the Forest Products Laboratory to evaluate chemical treatments applied to the boxes to provide higher stacking strength under these adverse moisture conditions. Some of the early work on chemical treatments, already reported,[3] showed that phenolic resins were among the more promising chemicals. This present report summarizes results of additional chemical treatments for high humidity conditions and treatments' that might improve the compressive strength when boxes are subjected to water-soaking.

Two different problems are involved: (1) What to use to keep out the moisture vapor and (2) what to use to hold out the liquid water. A number of chemicals, such as the waxes and silicone compounds, can and are being used for holding out water in many paper products, but these materials do not necessarily provide high vapor resistance. While they will reduce the rate of vapor pickup, containers treated with them will have nearly the same strength as those made with uncoated material if left at a given moisture condition until equilibrium is reached.

Protective coatings are being applied to paper and paperboard packaging materials to protect not only against water, but gases, oils, greases, chemicals, and many organic solvents. These protective coatings include (1) hot melts, (2) solvent coatings, (3) emulsion coatings, and (4) extruded coatings. Some of these are being used presently in conjunction with fiberboard boxes for packaging fruit, vegetables, and frozen produce. The containers are usually dipped, sprayed, or brushed with the various types of protective coatings. Boxes treated with some of these protective coatings were evaluated at the Forest Products Laboratory in the preliminary study on improving top-to-bottom compressive strength at high humidity. However, little or no improvement in strength was noticed beyond that obtained by adding more fiber to the components used in making the box. Many of these treatments added as much as 35 to 40 percent to the weight of the container, thus increasing the cost of shipment.

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[3] Fahey, D. J. Use of Chemical Compounds to Improve the Stiffness of Container Board at High Moisture Conditions. Tappi, 45 (9): 192A-202A, 1962.

The chemicals investigated in the study reported here were principally those that could be applied during the manufacture of the board. Most of the studies have involved treatments to linerboard which constitutes the facings of the corrugated box.

Materials and Treating Procedures

Linerboards for these investigations were made from a commercial-grade southern pine kraft pulp. The pulp was beater processed to about 575 milliliters Canadian Standard freeness. Chemical treatments were applied during the manufacture of the board by adding the chemicals to the pulp, applying them to the wet web at the smoothing press of the paper machine, or by treating the board at the size press. For most of the size press treatments, the moisture content of the board was 10 to 15 percent.

Chemicals have included thermosetting res ins, thermoplastic resins, starches, starch-resin combinations, latices, proteins, and water-repellent materials. These were generally applied following procedures recommended by the supplier. Weight of the board was usually maintained at approximately 42 pounds per thousand square feet, the same as the control. Therefore the fiber content of the boards to be treated was reduced by the amount of chemical applied to them The chemical was based on the weight of the moisture-free treated board.

Preliminary trials of selected chemicals were usually conducted on 8- by 10-1/2-inch sheets of linerboard. For these, 34- and 38-pound boards were produced from the same pulp furnish. They were preconditioned at 90 percent relative humidity to raise the moisture content of the board to about 15 percent, which was the same moisture content that the board would possess if it were treated at the size press of the paper machine during its manufacture. The horizontal size press of the paper machine was used for treating these sheets. The chemicals were added to the nip of the press and then the sheets were hand-fed into the press. They were then dried on a steam-heated drum to simulate the drying action of the paper machine,

The boards with the thermosetting resins were exposed in an oven at 220° or 300° F. for 15 minutes to make certain the resins were fully cured.

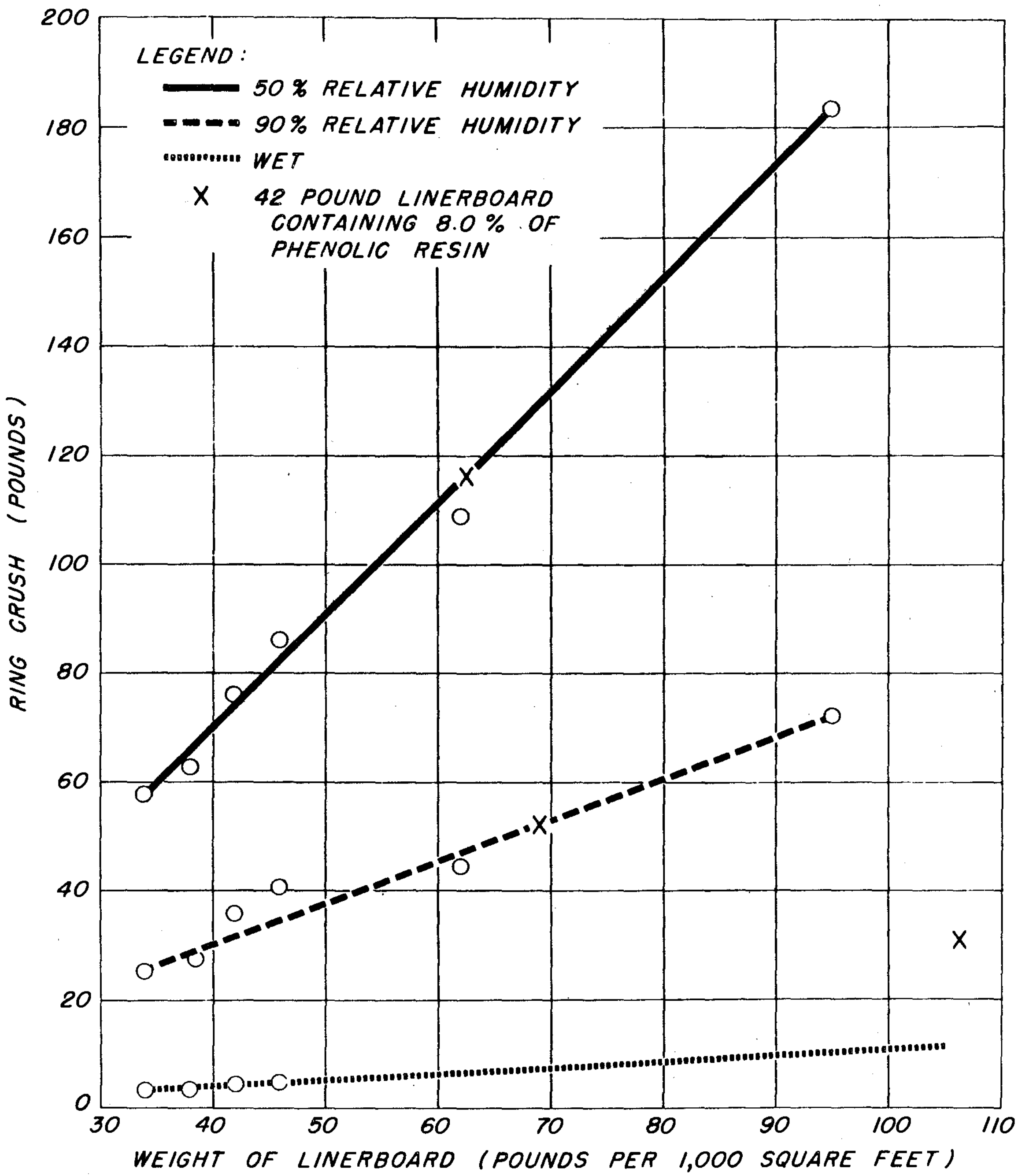


Figure 1.--Effect of board weight on the ring crush in the cross-machine direction of linerboard exposed to various moisture conditions.

Sheets representing the various treatments were conditioned at 50 percent relative humidity and 73° F. Strips 6 inches long and 1/2 inch wide were cut in each of the principal directions for ring crush. These specimens were exposed at 50 and 90 percent relative humidity, and in water at 73° F. for 48 hours. They were then tested for ring crush. Selected boards were tested for burst, tear, tensile, and folding endurance. All tests were made in accordance with TAPPI standard methods.

Results

Weight of Linerboard

Papermakers and box manufacturers have generally resorted to heavier components to make containers meet moisture problems. For instance, the box manufacturer, instead of using the 42-pound liner for the box, uses 52-, 69-, or even 90-pound liner.

Figure 1 shows the effect of increasing linerboard weight on cross-machine ring crush. At 50 percent relative humidity, the compressive strength increased rapidly with increases in board weight. At 90 percent relative humidity, strength noticeably improved with increase in weight. However, the compressive strength-to-weight ratio was not as high at high humidity as at the normal condition. To obtain a 60 percent increase in compressive strength, the box manufacturer would have to use 69-pound instead of 42-pound liners.

Examination of the strength after water-soaking obviously shows that additional strength cannot be achieved easily by adding fiber. For this severe condition, it is necessary to resort to a chemical treatment.

Thermosetting Resins

Phenolic resins were shown early to be promising for improving the compressive strength at high humidities. Research with these has continued in an attempt to achieve the best strength improvement with .the minimum loss in certain other properties that are considered essential in handling liners during fabrication into double-faced boards and into the final box. The phenolic resins have included those termed by the manufacturer as low-condensed or low-molecular weight type resins and those classified as medium-condensed resins.

Table 1.--Data[1] on southern kraft linerboards with phenolic or resorcinol resin for improving compressive strength

Resin		Weight		Ring crush, 6-inch specimen						Bursting strength	Tearing resistance		Average folding endurance (MIT)
Type	Amount	1,000 square feet	Square meters	50 percent relative humidity: Machine direction	50 percent relative humidity: Cross direction	90 percent relative humidity: Machine direction	90 percent relative humidity: Cross direction	Water soaked (48 hr.): Machine direction	Water soaked (48 hr.): Cross direction		Machine direction	Cross direction	
	Pct.	Lb.	G.	Lb.	Lb.	Lb.	Lb.	Lb.	Lb.	Pts.	G.	G.	Double-folds
BOARDS WITH NO TREATMENT[2]													
		41.3	202	105.8	78.5	44.9	32.4	4.0	3.0	94.0	255	295	380
WATER-SOLUBLE PHENOLIC RESIN APPLIED AT SIZE PRESS DURING MANUFACTURE OF THE BOARD[3]													
Medium-condensed (A)	5.9	42.1	205	160.1	118.7	72.4	52.6	50.5	31.5	114.0	166	222	59
	9.0	43.4	212	161.8	132.6	69.7	49.3	45.7	37.6	....	....	....	....
Medium-condensed (B)	8.8	43.1	211	147.8	115.4	69.2	49.8	....	19.6	116.0	108	168	44
	4.4	42.8	209	131.3	110.3	57.3	41.9	....	14.5	145.3	186	235	107
Medium-condensed (C)	4.9	44.9	219	160.7	116.5	61.2	49.3	....	....	111.0	272	301	135
Low-condensed (D)	[4]12.2	42.8	209	168.9	133.0	111.7	83.0	97.8	68.7	56.2	72	99	0
	9.6	44.3	216	186.0	150.9	105.5	85.7	61.3	53.3	59.1	82	109	0
Low-condensed (E)	8.2	42.7	206	155.6	123.7	100.1	74.4	62.5	51.3	61.6	82	107	0
Low-condensed (F)	5.5	41.5	203	146.0	95.7	70.0	39.0	40.7	23.5	99.6	128	177	7
WATER-SOLUBLE PHENOLIC RESIN APPLIED TO SINGLE SHEETS AT SIZE PRESS[3]													
Low-condensed (D)	8.0	39.9	195	129.0	102.8	69.7	53.5	53.6	34.7	....	....	....	....
Low-condensed (G)	10.6	41.3	202	130.9	104.4	84.0	63.0	60.6	41.0	....	....	....	....
Low-condensed (F)	17.1	43.4	212	....	127.4	....	77.9	....	60.0	....	....	....	....
Low-condensed (H)	20.0	42.7	209	155.6	115.9	95.6	72.5	75.8	48.7	....	....	....	....
	13.9	43.0	210	158.4	118.4	85.7	59.3	60.3	32.5	....	....	....	....
Low-condensed (I)	11.1	41.2	201	183.4	140.1	104.7	77.7	65.1	44.0	....	....	....	....
Low-condensed (J)	15.9	44.7	218	168.3	123.4	121.0	83.4	77.7	49.3	....	....	....	....
	7.4	41.9	204	140.3	106.9	87.1	62.5	53.1	39.4	....	....	....	....
RESORCINOL OR PHENOL-RESORCINOL RESIN APPLIED TO SINGLE SHEETS AT SIZE PRESS[3]													
Phenol-resorcinol[5]	11.8	42.2	206	201.6	155.0	109.9	81.5	63.3	44.0	....	....	....	14
Phenol-resorcinol[6]	12.4	42.5	207	189.9	149.3	96.9	75.0	41.6	34.8	....	....	....	185
Resorcinol	13.9	45.0	220	176.0	128.1	85.3	60.9	34.4	24.9	....	....	....	310

[1]Tests were made in accordance with TAPPI Standard Methods.

[2]Average of machine runs 5755, -56, -86, -87, -88, and 5847.

[3]Boards were exposed in an oven at 300° F. for 15 min. to cure the resin.

[4]Resin applied at the smoothing press.

[5]Mixture contains more phenol than resorcinol.

[6]Mixture contains more resorcinol than phenol.

As shown in table 1, the improvement in compressive strength varies with the type of phenolic resin. The low–condensed water–soluble phenolic resins generally have given the greatest improvement in ring crush, but this has been achieved with considerable embrittlement of the board, as noted by low folding endurance and tearing resistance.

The board containing 9.6 percent of a low–condensed phenolic resin (Resin D) had over twice as high cross–machine ring crush value at 90 percent relative humidity as the untreated control board tested under the same conditions. It was even stronger at 90 percent relative humidity than the control was at 50 percent relative humidity. It also possessed a very high ring crush value when wet. After 48 hours of soaking in water, the ring crush value was nearly equal to that for the untreated 42–pound control board tested at 50 percent relative humidity. This board had low folding endurance when the resin was cured. However, before cure of the resin, the board’s folding characteristic was similar to the untreated board.

The medium–condensed types of phenolic resins did not have so great an effect on folding endurance and tearing resistance. Resin B, for instance, lowered the tear about 25 to 35 percent as compared to as much as 65 percent for some of the boards treated with the low–condensed types of resin. However, the medium–condensed resins did not give as high ring crush.

The majority of the phenolic resins that have been used for treating boards require additional heat beyond that normally received during papermaking to develop the maximum wet compressive strength. Work has been directed toward accelerating the cure of the resin to reduce or shorten the heat treatment. One approach was the addition of resorcinol resin to the phenolic resin. Boards treated with such mixtures were found to require less time at a given temperature to cure the resin. The time and temperature could be reduced as the amount of the resorcinol resin in the mixture was increased. The compressive strength of boards treated with these mixtures high in resorcinol resin was considerably inferior to those containing phenolic resin. The folding endurance increased with increasing amounts of resorcinol, further indicating less embrittlement of the board.

The fact that additional heat is needed to obtain the maximum efficiency from the phenolic treatments may or may not be a deterrent to their use. With the resin in the “B”, or uncured stage, the board has properties more like untreated board. Combining the liners and the medium and the fabrication of the box can all take place before the resin is cured. The disadvantage, of course, is the problem with heat–treating the box to achieve the maximum efficiency from the treatment.

Table 2.--Data[1] on southern kraft linerboards with starch or starch-resin for improving strength

Type of starch	Crosslinking resin	Starch to resin ratio	Total amount applied	Weight: 1,000 square feet	Weight: Square meters	Ring crush, 6-inch specimen: 50 percent relative humidity: Machine direction	50 percent relative humidity: Cross direction	90 percent relative humidity: Machine direction	90 percent relative humidity: Cross direction	Water soaked: Machine direction	Water soaked: Cross direction
			Pct.	Lb.	G.	Lb.	Lb.	Lb.	Lb.	Lb.	Lb.
BOARDS WITH NO TREATMENT[2]											
				41.3	202	105.8	78.5	44.9	32.4	4.0	3.0
TREATED BOARDS[3]											
Ethylated potato		....	12.2	44.6	218	176.2	143.4	44.9	28.1	....	....
Ethylated corn		....	7.9	43.1	211	146.9	112.7	48.8	34.2	....	....
Ethylated potato	Low-condensed phenolic resin (F)	4:1	12.7	43.2	211	151.6	126.3	59.2	43.9	22.3	13.0
	Low-condensed phenolic resin (G)	4:1	14.2	42.6	208	157.5	131.0	69.9	49.7	43.9	31.5
	Low-condensed phenolic resin (K)	4:1	11.4	41.2	201	132.2	110.2	51.1	34.3	....	....
	Low-condensed phenolic resin (F)	2:1	14.2	42.6	208	157.5	131.0	69.9	49.7	....	....
	Medium-condensed phenolic resin (A)	6.6:1	11.4	40.7	199	140.3	112.9	44.9	32.0	....	....
	Polyamide resin	6.6:1	12.3	41.9	204	131.4	107.8	43.8	36.8	....	....
	Melamine resin	6.6:1	12.9	40.6	198	128.4	106.6	50.2	36.8	....	....
Ethylated corn	Low-condensed phenolic resin (F)	4:1	13.0	41.7	203	137.4	115.9	64.5	48.2	....	....

[1] Tests were made in accordance with TAPPI Standard Methods.

[2] Average of machine runs: 5755, -56, -86, -87, -88, and 5847.

[3] Chemical applied to sheets of 38-lb. board (machine run 5848) using the horizontal size press. Boards containing phenolic resin were exposed in an oven at 300° F. for 15 min., those containing polyamide and melamine resins exposed at 220° F. for 15 min.

The superior performance of the phenolic–resin–treated boards in contrast to boards treated with some of the other thermosetting resins is perhaps due to the higher moisture resistance of these resins and the high inherent compressive strength of the phenolic resins themselves.

Starch

Boards treated with starches are quite effective at normal conditions, but rapidly lose their compressive strength when the humidity is raised. Starches form good bonds, but these bonds weaken when exposed to high humidity.

Because starches are low in cost in comparison with the phenolic resins, work has been directed toward modifying the starches with other chemicals to provide a less moisture–sensitive bond. This technique has been used successfully in the past in starch adhesives. Resorcinol, urea, and glyoxolated compounds, which are used presently in conjunction with starch adhesives, were not too effective in improving the compressive strength of boards that were treated with mixtures of starch and these chemicals.

Some phenolic resins, particularly the low–condensed type resins, have been effective in improving the performance of both ethylated potato starch and ethylated cornstarch (table 2). A board containing about 14.2 percent of a mixture of 4 parts of starch and 1 part of phenolic resin had nearly the same compressive strength at 90 percent relative humidity as boards treated with some of the phenolic resins. However, after water–soaking, the phenolic–treated boards were superior to those boards treated with the starch–phenolic mixtures.

In most of the treatments with the starch–phenolic mixtures, the starch was first cooked following procedures recommended by the manufacturer, and the phenolic resin then addded to the cooked starch. However, comparable results were obtained with one phenolic resin by cooking the starch in the presence of the phenolic resin.

The ethylated starches have been used in most of this work because they can be cooked at relatively high solids. For example, to obtain a 12.2 percent treatment, a 25 percent starch mixture was required. With the oxidized or straight starches, it has not been possible to obtain this high a level of solids; therefore, the addition to the board of these starches has been correspondingly lower and so has the strength.

In most of the starch–phenolic resin treatments, the starch–to–resin ratio has been 4:1. However, limited treatments have been made with larger amounts of phenolic resins. A starch–to–resin ratio of 2:1 has given higher compressive strength at high humidity, but this raises the cost of the treating mixture and brings it closer to that for treatment with phenolic resin only.

Other Chemicals

A host of other materials were investigated, including melamine-formaldehyde and urea–formaldehyde resins, hydrocarbon resins, and latices. Results on boards treated with some of these are given in table 3. These data were obtained on sheets that had been treated with the various chemicals.

This particular melamine resin gave some improvement at 90 percent relative humidity, but no increase in compressive strength at the lower moisture condition. While the urea–formaldehyde resin treatment resulted in increases at 50 percent relative humidity, it did not improve the strength at 90 percent relative humidity. These thermosetting resins are generally less resistant to moisture than phenolic resins. This, undoubtedly, is one reason for the superior performance of the phenolic resin in imparting compressive strength to the paperboard.

Hydrocarbon resins were tried because of their lower cost in comparison with most of the thermosetting resins. While some of these treatments have increased compressive strength at the high humidity, for example hydrocarbon resin A in table 3, there was little or no increase with others, such as hydrocarbon resin B.

The different types of latex emulsions tried usually gave a lower compressive strength at the high humidity than a comparable weight of fiber. At the low humidity some of these, for example two acrylic copolymers, gave slight increases in ring crush. These materials in themselves are flexible and, when applied to paper or board, they impart a high degree of flexibility. For high compressive strength, rigidity is a more desirable property than flexibility.

Protein mixtures that have been studied have given high compressive strength at normal conditions, but treated boards rapidly lost their strength when exposed to high humidities. It was shown also that more of the original strength could be retained upon exposure to the high moisture by incorporating phenolic resin in the protein mixture similar to the method described earlier for starches.

Table 3.--Data[1] on southern kraft linerboards with various chemicals for improving strength

Chemical: Kind	Chemical: Amount	Weight: 1,000 square feet	Weight: Square meters	Ring crush, 6-inch specimen: 50 percent relative humidity: Machine direction	50 percent relative humidity: Cross direction	90 percent relative humidity: Machine direction	90 percent relative humidity: Cross direction
	Pct.	Lb.	G.	Lb.	Lb.	Lb.	Lb.
BOARDS WITH NO TREATMENT[2]							
		41.3	202	105.8	78.5	44.9	32.4
TREATED BOARDS							
Melamine-formaldehyde resin[3]	5.3	41.6	203	105.5	80.3	50.0	37.1
Urea-formaldehyde resin[3]	15.1	42.1	205	167.6	112.7	47.0	30.2
Hydrocarbon resin A	11.1	39.3	192	107.3	77.8	51.0	41.5
Hydrocarbon resin B	9.6	42.4	207	102.2	79.4	47.8	35.1
Vinyl-acrylic copolymer resin A	6.6	38.4	188	119.1	89.2	38.8	26.3
Vinyl-acrylic copolymer resin B	4.7	38.8	189	116.3	86.8	38.2	26.9
Polyurethane resin	11.0	39.1	191	99.4	66.1	37.1	24.2
Methyl-styrene emulsion	14.2	41.7	203	107.5	80.8	39.3	29.9
Butyl-latex emulsion	14.1	44.7	218	99.0	71.0	46.0	30.0
Protein phenolic resin mixture[4]	9.3	41.5	202	138.3	115.3	56.1	43.3
Carboxymethyl cellulose	1.2	37.6	184	99.1	70.1	38.3	27.1
Polyvinyl alcohol	2.2	37.8	184	122.0	87.0	37.3	26.6
Polyethylene glycol	27.1	47.1	230	55.3	40.2	12.4	8.0

[1] Tests were made in accordance with TAPPI Standard Methods.

[2] Average of machine runs 5755, -56, -86, -88, and 5847.

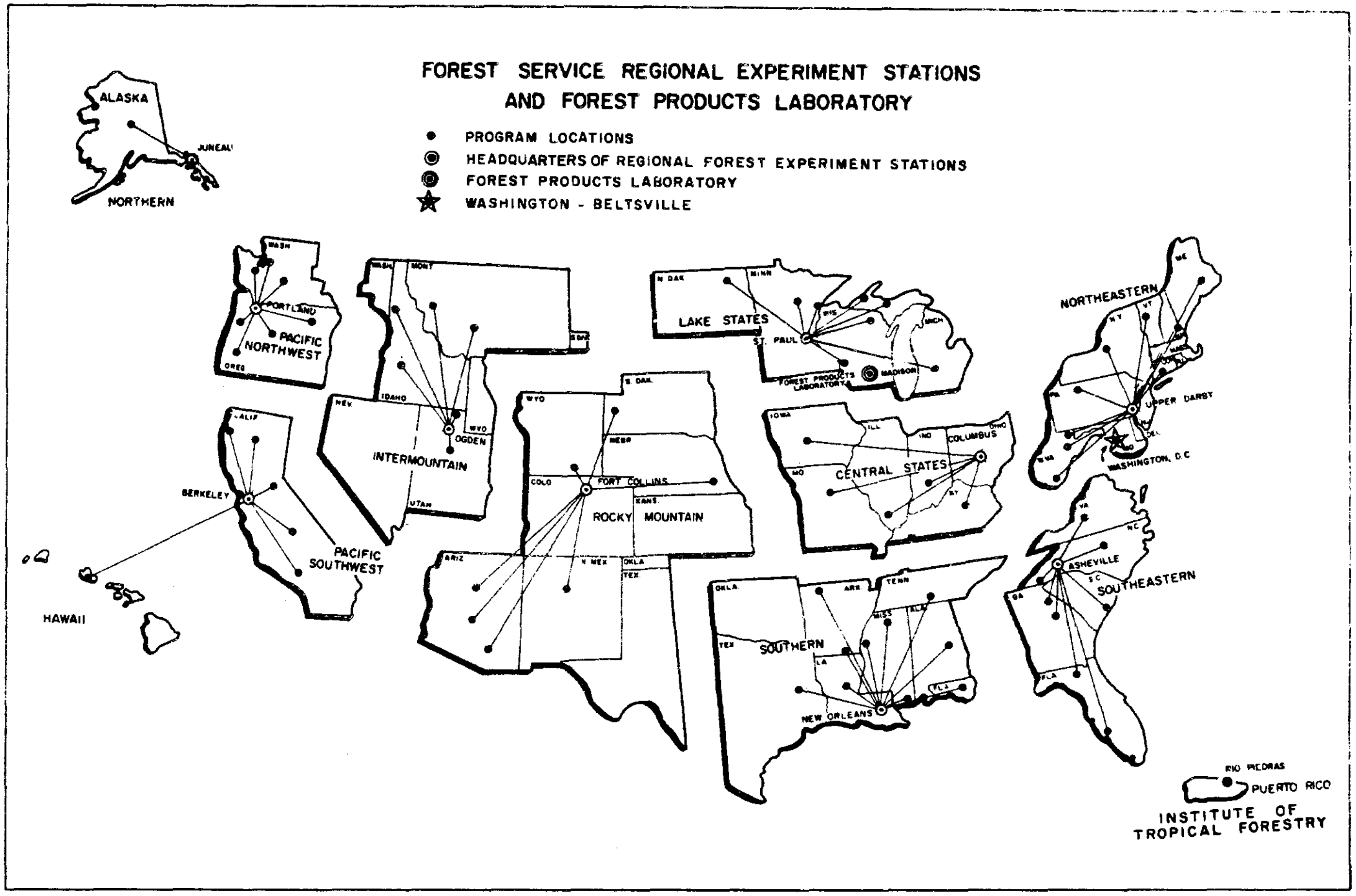
[3] Boards were exposed in an oven at 220° F. for 30 min. to cure the resin.

[4] Four parts of a hydroxyethylated wheat flour and one part low-condensed water-soluble phenolic resin (F). Board was exposed in an oven at 300° F. for 15 min. to cure resin.

Conclusions

Compressive strength of linerboard exposed to high moisture conditions can be improved by treatments with water–soluble phenolic resins. The low–molecular–weight type resins gave the higher compressive strength, but these also cause more embrittlement of the board than the medium–condensed phenolic resins.

Application of the chemical to the semidry board generally has been more effective in improving the compressive strength than adding the same amount of chemical to either the wet web or to the pulp stock used in making the board.



Forest Service regional experiment stations and Forest Products Laboratory