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PROJECT REPORT FORM

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EVALUATION OF EXPERIMENTAL BEATER ADDITION PHENOLIC RESINS FOR PAPER BASE LAMINATES

Introduction

This report is a continuation of the work covered under the general heading of liquid phenolic resins used as beater additives. It is concerned with the preparation of phenol-formaldehyde resins made at the Institute--their addition at the beater stage, the formation of sheets, and the evaluation of the pressed panels containing these resins.

The principal goal was to prepare a resin which when used as a beater additive would result in a laminated panel with characteristic properties of high density, low water absorption, good hardness with good resin retention. Since the degree of polymerization and type of catalyst are two of the factors influencing these properties in a resin, it was felt that by controlling the length of the cooking period the degree of linear linkage and cross-linking could be varied. Also, the removal of the acid catalyst was tried in order to lower the concentration of water-sensitive materials in the resin. Four modifications of phenol-formaldehyde resins were synthesized and tested.

The subsequent handling of the resins at the beater stage, during precipitation, etc. was identical for all four resins.

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Preparation of Phenol-Formaldehyde Resins

The apparatus used for the synthesis of the resins consisted of a 1000 ml., 3-neck flask fitted with a stirrer with a mercury seal, a water condenser with a straight tube, and a thermocouple well. The temperature was determined with an Alnor portable pyrometer fitted with a 28-gage chromel-constantan thermocouple. The heating was done with a bunsen burner. A water bath was used to cool the reaction when necessary.

Two-Stage Resin #64. The preparation of the resin is given in Project Report #22, which describes its evaluation as a wet-strength resin. See also, Project Report #21, which discusses two-stage resins.

Two-Stage Resin #70. The preparation of this resin differs from Resin #64, in that the acid-stage polymerization was lengthened to the point where a taffy-like consistency (indicating a fairly high polymer weight) was produced. The product produced by adding more formaldehyde and caustic and heating further, had a tendency to separate into two phases. The lower layer was a taffy-like resin, and the top was a fairly clear liquid. The addition of 20% NaOH was found to cause recombination of the two layers into a homogeneous liquid. A test was made to find the amount of 20% NaOH needed to adjust the water tolerance to suit beater addition needs. (A water dilution ratio around 2 to 3 appears to give a good resin emulsion in the beater.)

Two-Stage Resin #94: Formula:

1st Stage	2nd Stage
400 g. Phenol (liquid)	242 g. 37% Formaldehyde
242 g. 37% Formaldehyde	120 g. 20% NaOH
20 g. 20% H ₂ SO ₄	

The above mixture was heated slowly to 180°F., with constant stirring, and held there for one hour. The material separated into two phases. It was then cooled to 100°F. and the top layer poured off. An additional 242 g. of Formaldehyde, and 120 g. NaOH (20% dil.) were added. This was brought to 190°F. and held there for 20 minutes, and then cooled.

Two-Stage Resin #111. This resin has the same formula as resin #94. However, after the initial heating, the supernatant liquid was poured off, and the remaining resin was washed thoroughly with distilled water. The final cook was carried on for 40 minutes.

Three-Stage Resin #121. Formula:

A (1st Stage)	B (2nd Stage)	C (3rd Stage)
372 g. 100% Phenol	127.5 g. 20% H ₂ SO ₄	242 g. 37% Formaldehyde
28 g. water		120 g. 20% NaOH
242 g. 37% Formaldehyde		
88 g. 20% NaOH solution		

The mixture A was heated at 180°F. for 30 minutes (taking 30 minutes to reach 180°). It was cooled, and at 100°F., 127.5 g. 20% H₂SO₄ was added. The temperature was again raised to 180°F. and held there for 45 minutes. The second cooling brought about a phase separation. The supernatant liquor was removed and 242 g. 37% Formaldehyde and 120 g. 20% NaOH was added. The resin turned dark with the addition of NaOH. Heating at 180°F. was continued for 45 minutes. The product was then cooled with a cold water bath.

Three-Stage Resin #132. This resin was prepared by cooking resin #121 for 1.5 hours at 190°F. At the end of cooking, resin appeared considerably thicker than the original resin.

The resins were tested for per cent solids, pH, Brookfield viscosity, stroke-cure, gel-time, beater-stick point, and water dilution ratio:

Beater Addition of Resin

Crown Zellerbach unbleached sulfite with a Canadian standard freeness of 475 was used in the furnish on the basis of 60% pulp to 40% resin. The pulp was beaten in a master batch in a Noble and Wood five-pound laboratory beater to a freeness of 450 Canadian standard freeness. The pulp was dewatered in a centrifuge and then crumbed with the Institute pulp breaker. The consistency was 22.8%. Pulp from this master batch was used for each test.

The resin was added to 100 g. (O.D.) pulp which was adjusted to 3% consistency in a special mixer fitted with a spiral agitator.

The resins were precipitated with precipitant K (a mixture of 15 parts glacial acetic acid, 2 parts 85% phosphoric acid, and 83 parts distilled water) to a pH value of 4.5-4.8.

The stock was diluted to 3% consistency and mixed in a special spiral mixer. The resin was diluted with an equal volume of water and then added to the fiber--mixing was continued for 15 minutes, and the resin was then precipitated.

Sheet Formation

Sheets were formed, on the basis of 200#/24 x 36 x 500, from a stock-of .5% consistency (resin plus fiber) using an 8 x 8-inch recirculating sheet mold.

The sheets were wet-pressed between blotters at 65 p.s.i. and partially dried at 230°F. for three minutes. The sheets were then conditioned at 50% R. H. and 73°F. The sheets were weighed and the oven-dry weight calculated from the conditioned weight by oven drying one half sheet. The per cent volatiles was obtained by drying one sheet at 160°C. for ten minutes.

Pressing of Panels

Panels were pressed at 1000 p.s.i. at 300°F. for ten minutes. The per cent volatiles was found by the per cent loss in weight on heating a sheet for ten minutes at 160°C.

A material balance was made, and the completed panel was evaluated for density, Rockwell M hardness, and 24-hour water absorption.

Results

The resin characteristics are shown in Table I. The characteristics of Synco 721 (Snyder-Chemical Company) are given for comparison.

The resins functioned as well as the commercial resin, Synco 721, with which they may be compared. The retention in some cases was better than that achieved with the commercial resin. Two of the experimental resins were definitely unsatisfactory as brought out by their tendency to stick to the screen and to agglomerate into small lumps. See Table II. The material balances (Table III) were very good in only three cases. The rather high unbalance noted for run 751-127 and 751-99 is probably due to the failure to achieve equilibrium in the conditioned sheets or to some other factor not under control. The material

TABLE I
 EXPERIMENTAL RESIN PROPERTIES

Description	pH	% Solids	Viscosity, cps. 25°C.	Viscosity, cps. 50°C.	Stroke- Cure, Sec.	Gel Time Min.	Beater Stick pt.	Water Dilute Ratio
Synco 721	9.5	50.7 to 52.3	820	--	25	11.1	88°F.-100°F.	2.1 to 3.1
Two-Stage low mol. Wt.	--	43.3	--	--	90	14.9	low	0.3
Two-Stage, acid advanced	10.3	47.0	--	--	61	13.9	120	1.5
Two-Stage, acid removed	9.9	53.1	526	--	--	12.7	100	1.3
Two-Stage, Washed	9.4	51.3	6,160	1,320	17	27.0	118	0.4
Three-Stage	9.6	50.7	182	67	72	29.5	--	3.0
Three-Stage, Advanced	10.0	50.5	2,402	154	25	26.5	110	1.8

TABLE II
BEATER ADDITION OF EXPERIMENTAL RESINS

Furnish (40% Resin 60% Unbleached Sulfite Pulp)

Resin Type	g.(Solids)	Pulp Owendry, g.	Precipitant Type	pH	Canadian fiber basis	Freeness, fiber + resin basis	Drainage Time, sec.	% Retention A	% Retention B
8-84 Synco 721	-72.8	109.1	K	4.8	--	--	--	60.3	67.0
IPC 751-64	Resin did not disperse well. Discontinued.								
IPC 751-70	66.5	100	K	4.6	--	--	60	55.7	63.5
IPC 751-94	76.3+1.06g. NaOH	115	K	4.8	--	490 c.s.	21	60.5	66.0
IPC 751-111	77+1.5g. NaOH	115	K	4.5	--	--	23	66.5	79.1
IPC 751-121	77+1.5g. NaOH	115	K	4.6	--	--	12	11.6	12.9
IPC 751-132	77+2.2g. NaOH	115	K	4.7	380	520 c.s.	26	58.5	69.7

ets 8 x 8 inches

$$A = \frac{\text{Wt. of O.D. Sheets + freeness sample}}{\text{Wt. of resin solids}} - \frac{\text{Wt. of fiber}}{\text{Wt. of fiber}} \times 100$$

$$B = \frac{\text{Wt. of O.D. Sheets + freeness sample + Suspended solids}}{\text{Wt. of resin solids}} - \frac{\text{Wt. of fiber}}{\text{Wt. of fiber}} \times 100$$

TABLE III

MATERIAL BALANCE

Experimental Resins Added to Unbleached Sulfitc

Furnish (A)	Resin type	Wt. Resin (Solids) g.	Pulp (O.D.) g.	Precipitant X (Nonvolatiles) g.	Total input g.	Sheets (O.D.) g.	Wt. of freeness sample, g.	Recovered (B)			
								Suspended	Loss to Whitewater, g.	Total recovered g.	
Synco 721		72.8	109.1	3.78	185.68	153.0	--	4.80	27.1	184.9	-0.0
IPC 751-70 (2-Stage)*		66.5	100.0	1.1	167.6	137.00	--	5.16	10.15	152.3	-9.1
IPC 751-94 (2-Stage)**		76.3 (+1.06g. NaOH)	115.0	1.0	193.4	158.11	3.0	4.3	42.5	207.9	+7.5
IPC 751-111 (2-Stage)***		67.0+(1.5g. NaOH)	115.0	1.1	184.6	159.5	--	8.50	22.5	180.5	-2.2
IPC 751-121 (3-Stage)		70.9	115.0	.7	186.6	114.5	8.7	0.92	39.9	164.0	-12.1
IPC 751-132 (3-Stage)****		77.0+(2.2g. NaOH)	115.0	1.8	196.0	152.02	8.0	8.58	27.74	196.3	+0.2

removed

1 stages

or third stage

balance for the sticky resins, 751-64 and 751-121 were poor. However, the material balances are close enough in some cases, so that the estimation of retention of resin may be reasonably accurate.

The panel strengths are not unusually high. The impregnated sheets produced panels with greater hardness than the panels formed from beater-added sheets. However, the water absorption of the impregnated sheets was appreciably higher. A little closer control over resin content would be desirable in order to substantiate this difference. See Table IV.

Panels 751-137 and the two panels made up of impregnated sheets were the best in appearance being lighter in color and more uniform.

The two-stage resins gave the lowest water absorption results and the greatest density. Washing the resin in between stages seemed to help.

The best retention (79.1%) was obtained with a two-stage resin which was washed between stages. The next best was with the three-stage resin with the longest cook. In no case was the retention much better than achieved with the commercial resin.

Conclusions

Several experimental liquid phenol-formaldehyde resins were prepared and evaluated as beater additives for paper base laminating.

TABLE IV

PAPER BASE LAMINATES MADE WITH EXPERIMENTAL RESINS

Panel No.	Resin No.	% Resin in Sheets Added	% Volatiles	Hockwell M Hardness	Specific Gravity	% Water Absorption (24 hr.)
51-79	IPC 751-64	40.0	--	Delaminated	--	--
51-83	IPC 751-70	40.0	7.5	89	1.44	5.5
51-99	IPC 751-94	40.0	8.0	94	1.41	3.9
51-115	IPC 751-111	36.8	6.8	91.2	1.37	4.5
51-127	IPC 751-121	38.1	5.8	Badly pilled	--	--
51-137	IPC 751-132	40	5.7	91	1.25	4.35
1-104 Impregnated	IPC 751-94	--	4.6	97	1.28	8.43
1-108 Impregnated	IPC 751-94	--	4.7	100	1.32	13.2
4-105	Synco 721	40	8.2	71	1.36	8.9

te: Panels pressed at 1000 p.s.i. at 300° F. for 10 minutes.

The results in general, indicate a slight superiority in some cases over the commercial resin, Synco 721, as to the per cent retained. The differences are small and it is difficult to predict their validity except by actual practice.

The reactivity of the Synco 721 (Snyder Chemical Company) appears to be somewhat greater than most of the experimental resins. It should be noted that the measures of reactivity are rather crude and subject to operator techniques. This may be the explanation for one experimental resin having a lower stroke cure time but higher gel time than the control resin.

The two-stage polymerization technique allows for greater control over water dilution ratio than possible with a single-stage alkaline catalized resin.

Washing out the acid catalyst between stages appears to aid in lowering the 24-hour water absorption by the finished panel.

Polymerization in three stages does not improve the mechanical characteristics. Apparently the initial polymerization under highly alkaline conditions serves in the same manner as the acid cure stage which serves to carry the resin toward the water insoluble stage. The final alkaline polymerization increases the viscosity possibly by increasing the polymer molecular weight.

The over-all appearance of the panel made with the three-stage resin seemed lighter and more uniform than the rest of the panels.

These resins show that too low a molecular weight tends to cause pilling of the resin and sticking on the screen. Advancing such a resin either during the acid or alkaline stage reduces the stickiness of the resin.

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PAPER BASE LAMINATES (Beater Addition of Durez #15535 Resin)

INTRODUCTION

For the past few years the Institute has been carrying on a general investigational program for the purpose of studying paper base laminates. This study has included laminates formed by both methods of impregnation and beater addition. The main features of interest have been the action of the resin during the formation of the sheets, and ultimately the evaluation of the pressed panel.

Recently, a great deal of interest has centered around the liquid phenolic resins as beater additives. The Durez Plastics and Chemicals, Inc. submitted for evaluation a sample of a resin #15535, which they felt showed unusual characteristics as a beater additive resin. Along with the sample they included a series of procedures recommended for handling Durez #15535.

MATERIALS AND PROCEDURES

Crown Zellerbach unbleached sulfite-pulp with a Canadian Standard Freeness of 475 has been used as the base stock throughout this investigational work. Two different precipitating agents were used to precipitate the resin-- one contained 75 grams glacial acetic acid and 5 grams H_3PO_4 diluted to one liter. The other precipitant was a 12% solution of $Al_2(SO_4)_3 \cdot 18H_2O$.

Enough water was added to the pulp to make a 3% consistency stock mixture. This was beaten in a special spiral beater for 2.5 hours, and 40% (basis of furnish) Durez #15535 resin, which had previously been diluted to 25% solids, was added. Beating was continued for 1/2 hour; then, in one case, enough sodium aluminate was added to reduce the pH to 4.4. In the other, a mixture of 75 grams glacial acetic acid and 5 grams phosphoric acid diluted to one liter was added to a pH of 4.6

This stock was then diluted to 0.5% consistency and sheets were formed on basis of 200#/24 x 36/500. The white water was recirculated. The sheets were wet pressed at 65 p.s.i., partially dried for three minutes at 245°F. The sheets were then conditioned at 50% R.H. and 73°F.

Panel pressing was done at 300°F. -- 1000 p.s.i. and maintained for ten minutes.

The finished panel was evaluated for density, Rockwell M hardness, and 24 hour-water absorption:

RESULTS

The following table will serve to facilitate an evaluation of the various precipitating agents used with Durez R-11 15535. In each case the only change in procedure was in the type of agent used to precipitate the resin.

TABLE I
Evaluation of Durez 15535 Beater Addition Resin

		Precipitating Agent			
		75 g. Glacial Acetic 5 g. Phosphoric diluted to 1 liter	$Al_2(SO_4)_3 \cdot 18 H_2O$ (12% sol.)	Na Aluminate to pH 10 12% sol. of alum to pH 4.4	
1. pH after precipitation		4.6	4.4	4.4	
2. Drainage time, sec.		44.0	66.2	15 ⁺ minutes	
3. Per Cent Resin Retention.	Method A*	54.9	72.1	Stock appeared somewhat colloidal -- extreme length of drainage time made it expedient to discontinue forming sheets.	
	Method B	60.3	82.9		
4. % Volatiles		6.7	8.1		
Panel Evaluation	Density g/cc	1.22	1.40		
	Rockwell M Hardness	88.1	88.3		
	24 hour water absorption, %	4.04	5.3		
	C. S. Freeness (resin + fiber Basis)	540	320 cc.		
Panel Dimensions, cm.		17 x 15.9 x .254	16.6 x 16.6 x .259		

Note: Furnish - Crown Zellerbach Unbleached Sulfite - 60%

Durez Resin 15535 - 40%

*A - $\frac{\text{O.D. sheets} - \text{Wt. O.D. fiber}}{\text{Resin solids added}} \times 100$

B - $\frac{(\text{O.D. sheets} + \text{white water susp. matter}) - \text{Wt. O.D. fiber}}{\text{Wt. Resin solids}} \times 100$

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USE OF I.P.C. RESIN 751-64 (LIQUID PHENOLIC)

AS A WET STRENGTH RESIN:

The feasibility of using liquid phenolic resins for wet strength has been previously tested and found to be unsatisfactory.

The possible use of a low molecular weight phenol-formaldehyde resin of limited water solubility seemed theoretically valid. Such a resin was polymerized by the two-stage technique and evaluated as a wet-strength resin. The feasibility of getting an improvement in dimensional stability with such a resin was also tested.

PROCEDURE

Synthesis of Phenolic Resin

The resin used in this work was prepared in a one-liter, three-neck flask fitted with a stirrer, condenser and thermocouple.

The first stage was carried out at 145-180°F. until a flocculent precipitate was formed. The following materials were used:

First Stage

400 grams	Phenol (liquid) 92-94% solids
242 grams	Formaldehyde (37%)
20 grams	20% sulphuric acid

Second Stage

120 grams	20% NaOH
242 grams	Formaldehyde

The product from the first stage was cooled and the other materials were added.

The temperature during the second stage was slowly advanced to 194°F. in a little over an hour then the product was cooled and collected. The beater stick point was found to be too low to measure and the water dilution ratio was less than 1. The solids content was 43.3%.

Beater Addition of Resins

The resin was added to a bleached kraft stock which had a Canadian standard freeness of 520 and was at a consistency of 2.1%. Several batches were prepared to give approximately 0, 3, 5, 10 and 25% resin. The resin was mixed with the pulp in a special mixer fitted with a spiral agitator. The mixing was continued for about an hour to assure good contact between fiber and resin.

Sufficient precipitating agent was added to drop the pH to about 4.5. The precipitant was made up as follows:

Precipitant

100 grams $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Papermakers alum)
40 grams conc. H_2SO_4
Water to make 1 liter.

The Canadian standard freeness was taken after the stock had been diluted to a consistency of 0.3%. The stock was diluted further in the deckle box in the sheet forming operation.

Handsheet Preparation

Handsheets were prepared using the 0.3% stock in an 8 x 8-inch sheet mold. The wet sheets were pressed between wet blotters at 65 p.s.i. for three minutes and then dried at 215°F. for about fifteen minutes on a steam-heated copper cylinder. Specimens from each batch were given an additional one minute cure at 350°F. in an air circulating oven.

Testing

The prepared sheets were conditioned at 50% R.H. and 73°F. and tested for basis weight, wet and dry tensile, and Neenah hygroexpansivity. The per cent of hygroexpansivity was determined from the change in length in going from equilibrium at 75% R.H. to equilibrium at 33% R.H. The sheets were preconditioned at 50% and 86% R.H. for the hygroexpansivity tests.

Results

The results are given in Table I and Figures 1, 2, and 3. Table I gives the average test results for basis weight, Schopper wet and dry tensile, and Neenah hygroexpansivity.

Figure 1 gives the wet strength as a per cent of the dry strength for cured and uncured sheets containing different amounts of resin. It can be seen that the resin appears to impart appreciable wet strength with increased resin content. There is a slight improvement in wet strength in the uncured sheets. The wet strength of the cured sheets, however, is much greater than the wet strength of the uncured sheets.

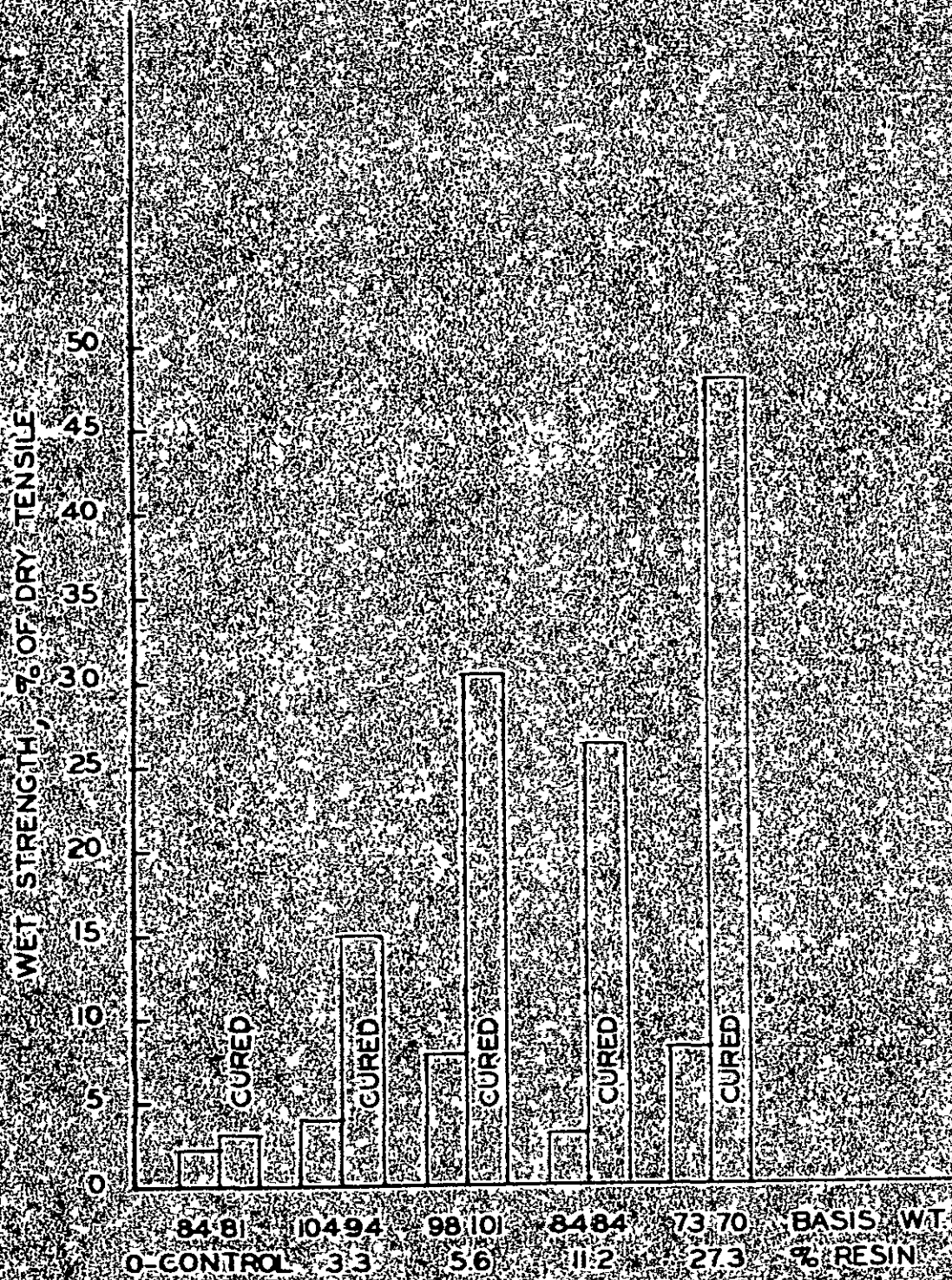


TABLE I

Beater Addition of Liquid Phenol-formaldehyde Resin

Effect of I.P.C. Resin No. 751-64 on Wet Strength and Hygroexpansivity of Bleached Kraft

No.	Code	% Resin (fiber basis)	Basis Wt. lbs. (500-75x40)	Schopper Tensile Strength lbs./in.		Wet Strength (% of Dry)	% Hygroexpansivity (Neenah)
				Dry	Wet		
1.	Control 751-92-2 Uncured	None	83.7	22.3	0.5	2.2	0.415
2.	Control 751-92-2 Cured	None	81.2	25.9	0.8	3.1	0.395
3.	751-90-1a uncured	3.3	38.5	15.6	0.9	5.8	0.475
4.	751-90-1a cured	3.3	39.0	15.5	2.8	18.0	0.440
5.	751-90-1 uncured	3.3	104.9	42.5	1.7	4.0	0.530
6.	751-90-1 cured	3.3	94.3	42.3	6.3	14.9	0.520
7.	751-91-1 uncured	5.6	97.7	42.9	3.4	7.94	0.495
8.	751-91-1 cured	5.6	101.2	47.8	14.6	30.5	0.480
9.	751-91-2 uncured	11.2	83.5	28.9	0.9	3.1	0.475
10.	751-91-2 cured	11.2	84.2	34.2	9.0	26.3	0.395
11.	751-92-1 uncured	27.3	73.3	35.3	2.9	8.2	0.410
12.	751-92-1 cured	27.3	69.7	37.2	17.8	47.9	0.445

Figure 2 shows the wet and dry tensiles at various resin contents for cured and uncured sheets. There is little difference between the dry tensile of cured and uncured sheets. The one minute cure at 350°F. causes an appreciable improvement in wet tensile of the resin-containing sheets. The one minute cure did not alter the wet strength of the control sheets significantly.

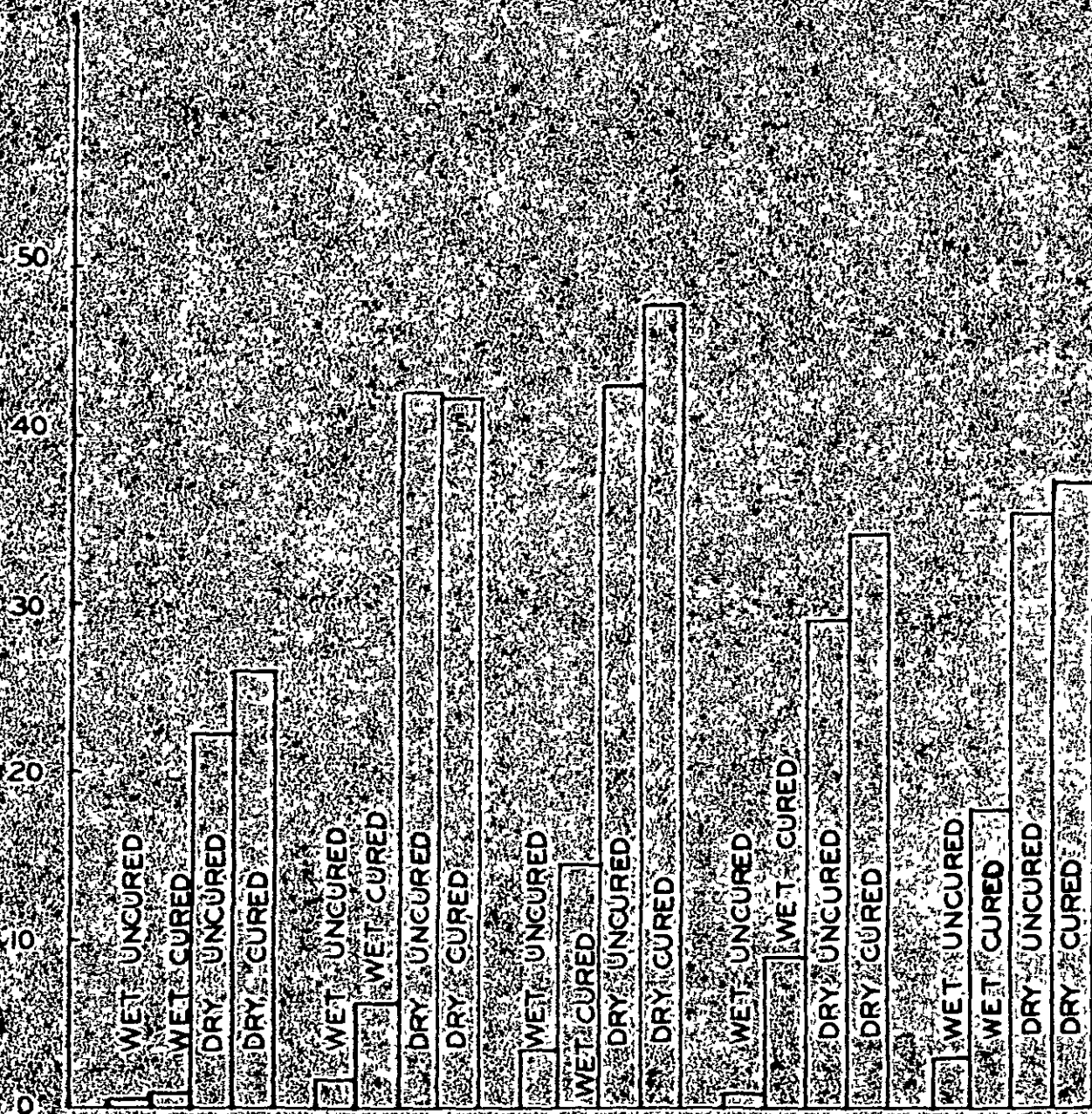
Figure 3 shows the effect of resin on hygroexpansivity. Apparently a low resin percentage actually harms the dimensional stability of the paper. The hygroexpansivity figures for the control appear a little low for a beaten sheet of this basis weight according to a comparison with bleached sulfite. The basis weights are given in lbs. per ream (500 - 25 x 40).

Discussion

The value of a phenol-formaldehyde resin for wet strength improvement is probably limited to special applications. The degree of wet strength achieved with The Institute of Paper Chemistry resin 751-64 is low as compared with melanine-formaldehyde and newer urea-formaldehyde type resins. Also the cure conditions required for the phenolic would not be achieved on a normal paper machine due to the limitations for heating at the usual machine speeds. The cure requirements could very likely be lowered through the incorporation of small percentages of resorcinol in the resin formulation.

The advantage of a phenol-formaldehyde wet-strength resin would probably be in applications requiring acid resistance.

WET AND DRY TENSILE (LBS./IN.)



0 - CONTROL

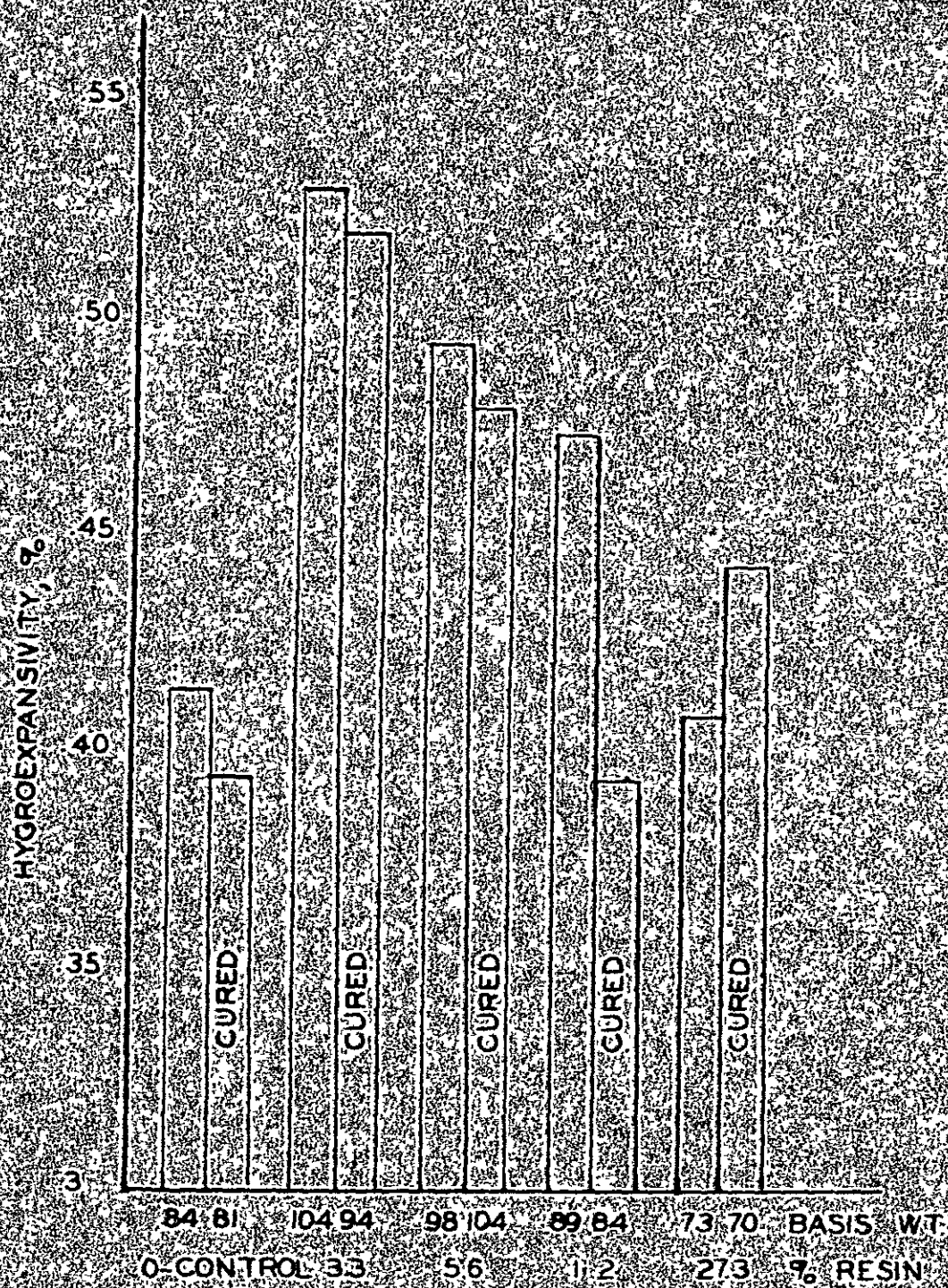
33

56

112

273

% RESIN



The cost of a phenol-formaldehyde resin would probably be higher than that of a urea-formaldehyde resin since urea sells for 5-1/2 cents per pound as compared with 19 cents per pound for phenol on today's market.

For comparison purposes Table II is given showing the wet strength achieved by Rohm and Haas with their latest beater addition resin Uformite 700 plus 1% rosin size.

There was no difficulty noted in the use of the I.P.C. resin No. 751-64 at the percentages discussed. At 67% resin (on a fiber basis) pilling and sticking to the wire was noticed.

The effect on dimensional stability was in the wrong direction according to the results observed in this study. However at the 11.2% (cured) resin content the dimensional stability was lower than the control without cure and equal to the control which was given a one minute heat treatment at 350°F.

TABLE II

WET STRENGTH OF BLEACHED SOUTHERN KRAFT*

Furnish Catalyst: 3% alum, then H₂SO₄ to pH 5.0

Size: 1% Rosin

Basis Weight: 35 lbs. laboratory handsheets

Uformite 700 % Resin (fiber basis)	Tensile Strength (28 days cure) lbs./in.		Wet Strength (% of Dry Tensile)
	Dry	Wet	
0.25	18.3	2.1	11.5
0.50	16.8	2.8	16.7
1.00	18.3	3.7	20.2
1.50	20.5	4.5	21.9
2.00	20.6	6.2	28.7
3.00	21.8	7.0	32.1

*Data from Rohm and Haas Bulletin on Uformite 700.

Conclusions

The use of I.P.C. resin 751-64 has been shown to develop appreciable wet strength to a bleached kraft. With 5.6% resin on a fiber basis the wet strength was approximately 30% of the dry strength. The resin required an additional cure of one minute at 350°F. in order to achieve the wet strength in the paper.

The hygroexpansivity was increased with a low resin content in the paper but additional resin to about 11% appeared to lower the hygroexpansivity to a value equal to that of unmodified paper. A further increase in resin content appeared to cause an increase possibly due to an inadequate cure of the resin.

The value of a phenolic wet strength paper would probably be limited to applications requiring acid resistance since the cost would probably be higher than the more efficient commercially produced urea-formaldehyde and melamine-formaldehyde resins.

fv/mm

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Study of Beater Addition Resins
Development of a Two-Stage Phenol-Formaldehyde
Beater Addition Resin

Introduction

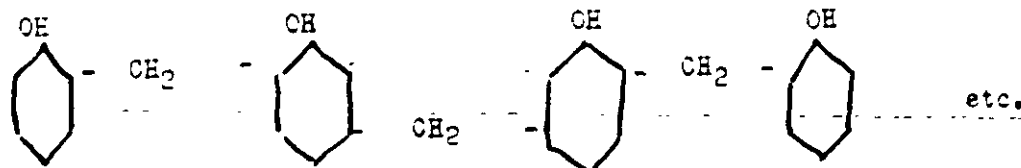
Until recently it has not been too satisfactory to use phenol-formaldehyde resins in beater addition to paper. The Snyder Chemical Company, however, has developed special resins which are claimed to show unusual retention on the fiber with practically no loss to the white water. These resins are claimed to be fast curing and can be molded or laminated after addition to papermaking fibers and formed into paper on regular papermaking equipment.

According to unpublished reports, however, the retention was not as good as the appearance of the white water would indicate. Also the flow of the resin-filled paper was inadequate at low pressures for some purposes.

The objective of this project was to study the synthesis of phenolic resins and to try to improve the retention and flow by a new technique for polymerization. Theoretically, the polymerization under acid conditions tends to form methylene linkages- especially if lower ratios of phenols are employed. This type of linkage may be pictured as a long chain of phenolic groups connected by methylene

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groups possibly as follows:



A long chain polymer tends to be more easily fused than a cross-linked polymer of equivalent molecular weight.

Under alkaline conditions the reaction is somewhat different with a greater tendency for cross-linking in a very complicated series of reactions which are not too well understood.

By forming a resin in two stages of polymerization it was felt that the molecular structure could be controlled somewhat to make the product more suitable for the intended use of beater addition. This appeared to call for an acid stage polymerization to obtain maximum flow followed by an alkaline reaction to obtain hardness and a fast cure.

Two-stage resins were successfully polymerized with laboratory equipment in small amounts and were evaluated as "beater" additives by comparing their behavior with Snyder Chemical Company's Synco 721.

Procedure

Synthesis of Experimental Resins

Three widely differing resin solutions were prepared by phenol-formaldehyde condensation using the same proportions of

phenol and formaldehyde by varying the degree and conditions for polymerization.

The laboratory-scale resin production was carried out in a Pyrex glass resin reaction vessel of four liters capacity. The vessel was fitted with a Lightnin¹ variable-speed stirrer, straight tube water-cooled condenser, 0-200°C glass thermometer and a glass stoppered port for sampling. Ground glass connections were used at all joints. The vessel was heated with a Glas-col mantle regulated with a variable voltage transformer. The mantle could be substituted by a cold water bath for cooling.

Resin No. 751-27

The following materials were placed in the reaction vessel in the order given:

1000 grams Phenol (92- to 94%)
605 grams Formaldehyde (37%)
50 grams Dilute sulfuric acid (20%)

The voltage on the mantle was adjusted so that the rate of heating was not too high. An attempt was made to hold the temperature at 60°C. but the lag in heating and cooling caused rather wide fluctuations in temperature.

This material was polymerized to the point where a definite phase separation was observed after an hour of heating at 60 to 80°C. The reaction was continued for another twenty-two minutes at a temperature varying between 71°C. and 86°C. Three hundred grams of a 20% NaOH solution in water were then added. This

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dissolved the resin to form a clear solution. The temperature was dropped to 40°C, and 605 grams of a 37% (by weight) solution of formaldehyde were added at this point. A sample of the mixture was taken and found to have a dilution ratio of 0.8. (This is the ratio of weight of water that must be added to give a turbid appearance to the weight of resin solution used.)

This mixture was then reacted at a temperature ranging from 65°C, to 73°C. The dilution ratio at the end of an hour was 1.1. The reaction was stopped by cooling the vessel with cold water.

The product had a viscosity of 69. centipoises at 34°F. and 236 centipoises at 59°F. at 47.4% solids content. It had a stroke cure time of 29.5 seconds at 300°F.

The pH of the finished resin solution was 9.5 as measured with the Macbeth line-operated pH meter.

The resin had a "stick point" (see Appendix for test method) which was too low to be measured by the usual techniques.

Resin No. 751-46

This was prepared with the same proportions of phenol and formaldehyde as No. 751-27, the difference being that it was advanced to a greater extent during the last or alkaline stage. The resin was heated two additional hours by raising the temperature gradually from

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60°C, to 90°C. This product had a dilution ratio approaching zero as practically no water of dilution could be added without causing turbidity.

In order to get a measure of the "stick point" the resin was solubilized by adding 0.6 gram of 10% NaOH. This gave a "stick point" of 49.4°C.

Resin No. 751-32

This resin was prepared with the same proportion of phenol and formaldehyde as the others. The reaction, however, was extended during the acid stage to give a higher molecular weight before introducing the caustic and additional formaldehyde. The final stage was reacted for approximately one hour. The product was very viscous having the consistency of a very soft taffy. This was thinned by adding 128 grams of 20% NaOH. The pH was 9.5 and the "stick point" was 45°C. The dilution ratio was greater than 5. The solids content was 46.5%.

Control (Synco 721)

This was a fresh lot of resin with 50.7% solids. The water dilution ratio was 2.1. The "stick point" was 31°C, and the pH was 9.45.

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Stock Preparation

A five-pound master batch of bleached sulfite was beaten to 368 Canadian Standard Freeness in the Noble-Wood beater.

The equivalent of 102 grams of oven-dry pulp was used for each trial. The dewatered pulp was diluted to 3% consistency in a special mixer fitted with a spiral agitator to minimize stapling.

The equivalent of 63 grams of resin solids was added after diluting the resin solution with an equal weight of water. (The resin was adjusted with dilute (10%) NaOH in runs No. 52, No. 54 and No. 58 to permit dilution). The pulp and resin were slurried for about fifteen minutes in order to get good dispersion and intimate contact between the resin and the fibers. The resin was then precipitated by adding an acidic precipitant (Precipitant K)* to lower the pH to 4.5 to 4.8. The mixing was stopped shortly after the precipitant had been well dispersed (about one minute in the laboratory mixer).

Sheet Formation

The stock was then diluted to 0.5% fiber plus resin consistency with distilled water and used in making 8 by 8 inch sheets. The theoretical basis weight was approximately 200 pounds per ream (24x36-500). The stock was further diluted to about 0.1%

*Precipitant K

150 grams	Glacial Acetic Acid
20 grams	85% Phosphoric Acid
Water to make 1 liter	

consistency in the sheet mold using recirculated white water.

The white water was tested for dissolved and suspended solids in order to obtain information on material balance.

The wet sheets were pressed between moistened blotters at 65 psi and then partially dried by heating for three minutes at 245°F, on a Williams curved copper faced electric drier fitted with a glass cloth cover. The moist sheets were then conditioned at 50% R.H. and 73°F. The conditioned sheets were weighed in order to obtain information for a material balance.

Laminating and Testing

The sheets were conditioned at 50% R.H. and 73°F. until the weight was fairly constant (within 0.2 gram). This usually required from three to five days. One sheet was then divided in two and used to obtain the percent volatiles* and the oven-dry weight.

The rest of the sheets were then laminated into a panel at a pressure of 200 psi for ten minutes at 300°F. The press was loaded hot and unloaded cold in order to minimize distortion.

The panel was trimmed and the specific gravity was determined from the weight and dimensions.

*See appendix

Table I.--Characteristics of Experimental Beater Addition Resin

Resin	Description	% Solids	pH	Stroke Care	Dilution Ratio	Stick Point
Control Synco 721	Commercial Resin	50.7	9.45		2.13	31°C
751-27	Two-Stage Polymerization	47.4	9.60	29.5	0.4	very low
751-32	Two-Stage Acid Advanced	46.6	9.50		>5.0	45°C
751-46	Two-Stage Alkaline Advanced	49.5	9.45		<0.5	49.4°C

Table II.--Material Balance "Beater" Addition of Resin

Run No.	Resin Type	Resin Solids	O.D. Pulp	Precipitant	Total Input	Wt. Sheets O.D.	Loss to White Water	Total Re-covered	% Re-tent	
		Grams	G.	Grams	Grams	Grams	Grams	Grams	Grams	
Control 49	Synco 721	68	102	.85	170.9	130.3	12.2	28.4	170.9	59.6
Control 57	Synco 721	68	102	.83	170.8	134.7	--	--	--	--
35	751-27	68	102	.72	170.7	134.0	12.6	25.2	171.8	71.4
37	751-27	68	102	2.17	172.2	140.2	--	--	--	--
52	751-27+NaOH	68+1.43NaOH	102	1.51	172.9	132.3	9.1	31.9	173.8	58.7
53	751-27+NaOH	68+1.43NaOH	102	1.58	173.0	131.7	--	--	--	--
44	751-32	68	102	1.67	171.7	139.9	12.6	21.0	173.5	74.3
54*	751-46	68+.93NaOH	102	1.34	172.3	135.7	4.2	21.0	160.9	--

*The drainage was very slow with this stock.

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Table III.--Paper Base Laminates With "Beater" Added Resin

Panel No.	Resin Type	% Resin		% Specific Gravity	Rockwell M Hardness	% Water Absorption	Comments
		Added	Volatile				
Control 49	Synco 721	40	7.2	1.08	49	15	Poor bonding
Control 57	Synco 721	40	7.2	1.11	47	16	OK
35	751-27	40	8.9	1.00	32	17	Poor resin distribution
37	751-27	40	6.6	1.11	46	28	Poor resin distribution
52	751-27+NaOH	40	6.6	1.08	45	15	Poor bonding. O.K. distribution
58	751-27+NaOH	40	6.7	1.09	47	16	Poor bonding
44	751-32	40	7.7	1.12	51	14	OK
54	751-46	40	7.0	1.14	53	11	OK

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Results and Discussion

The resin characteristics are summarized in Table I.

It appears as though the characteristics of the experimental resins have bracketed those of the commercial resin in all aspects save the solids content. The solids content could undoubtedly be adjusted without too much difficulty. The pH ranged from 9.45 to 9.60; the dilution ratio from zero to over 5.0; and the "stick point" from a value too low to be significant to 49.4°C.

The material balance for the "beater" addition is shown in Table II. Only one of the experimental resins suffered as much loss in dissolved solids as found for the commercial resin. The same pulp was used in each case and distilled water was used throughout.

The retention figures shown are derived from the weight of the over-dry sheets plus the white water suspended solids assuming 100% fiber retention. The retention for run No. 54 is not given since the material balance was too far off to make the retention calculation valid. However, the white water solubles would tend to indicate that the retention should be quite comparable to run No. 44.

The resin distribution for the acid advanced resin appears to be slightly better than that of the commercial control. Photo micrographs of the blank fibers are shown in figure 1., the Synco 721 control in figure 2. and the acid stage advanced resin in figure 3. All were taken at X100 with bright field illumination.

The material balances appear to be fairly satisfactory in all but one case. In this instance the resin caused slow drainage and the sheets were held overnight between blotters. Apparently the transfer to the blotters was excessive.

The evaluation of the panels is shown in Table III. For this preliminary study the criteria used for evaluation are the specific gravity, Rockwell Hardness and twenty-four hour water absorption. At the low pressure used the differences achieved in specific gravity are not very great, in fact, the differences between duplicates is almost as great as the total range. The Rockwell Hardness test does appear to give significant differences. The lowest molecular weight experimental resins gave the poorest hardness. Improving the resin distribution by increasing the water tolerance through the addition of caustic seemed to help a little.

The more advanced resins gave the greatest hardness values. The highest value was for the resin which had been advanced on the alkaline side during polymerization in the reaction vessel. The next highest hardness was for the resin which had been advanced to the greater extent on the acid side.

The water absorption was high for the entire series. This is due largely to the very low laminating pressures used in pressing the panels. The best (lowest) water absorption was achieved with the two experimental resins which had been advanced to the greatest

degree during their production. The best water absorption was with an experimental resin which gave so slow a drainage that it would be impractical for commercial applications.

Conclusions

The objectives of this study were apparently achieved in that new beater addition resins of improved flow and retention have been synthesized by altering the conditions of polymerization. Larger scale tests would be indicated to ascertain the validity of the small scale laboratory findings.

The water tolerance has been found to be important in determining the resin distribution on the fibers. Too low a water tolerance appears to cause poor resin distribution. The water tolerance can be adjusted through the techniques used in polymerization and by the use of small amounts of caustic where the water tolerance is too low to permit good emulsification in the beater.

The "stick point" was found to be a valuable test for predicting "pilling" or resin agglomeration and sticking to the wire. However, by adjusting the water tolerance of a low stick point resin with caustic it was found that "pilling" and sticking are minimized.

The resin retention achieved was far from satisfactory. Further work in this direction, possibly using radioactive isotopes for studying degree of retention, would be very valuable.

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Appendix

Stick Point

Measure out 380 ml. of cold (40°F.) water into a 1000 ml. beaker.

Weigh out 10 grams of resin in a 100 ml. beaker. Add 10 grams of distilled water. Stir well to insure complete solution.

Add the diluted resin to the cold water. Washing out the small beaker with several small additions of water from a wash bottle. Stir at a constant rate.

The pH of the suspension is lowered to 4.0 with Precipitant K. The resin forms a very fine floc at this point and is kept in suspension by gentle stirring. Approximately 40 volts on a laboratory Lightning Mixer has been found to be satisfactory in our laboratory.

The beaker and its contents is heated gently (with a fairly full flame but with the air practically off).

The temperature at which the first tendency for the turbid suspension to clear is noted. The final temperature is noted when the suspension becomes clear.

Per Cent Volatiles

$$\% \text{ Volatiles} = \frac{\text{Conditioned Wt.} - \text{Wt. after 10 minutes at } 160^{\circ}\text{C.}}{\text{Conditioned Wt.}} \times 100$$



Figure 1.
Bleached Sulfite 368 C.S. freeness
X100

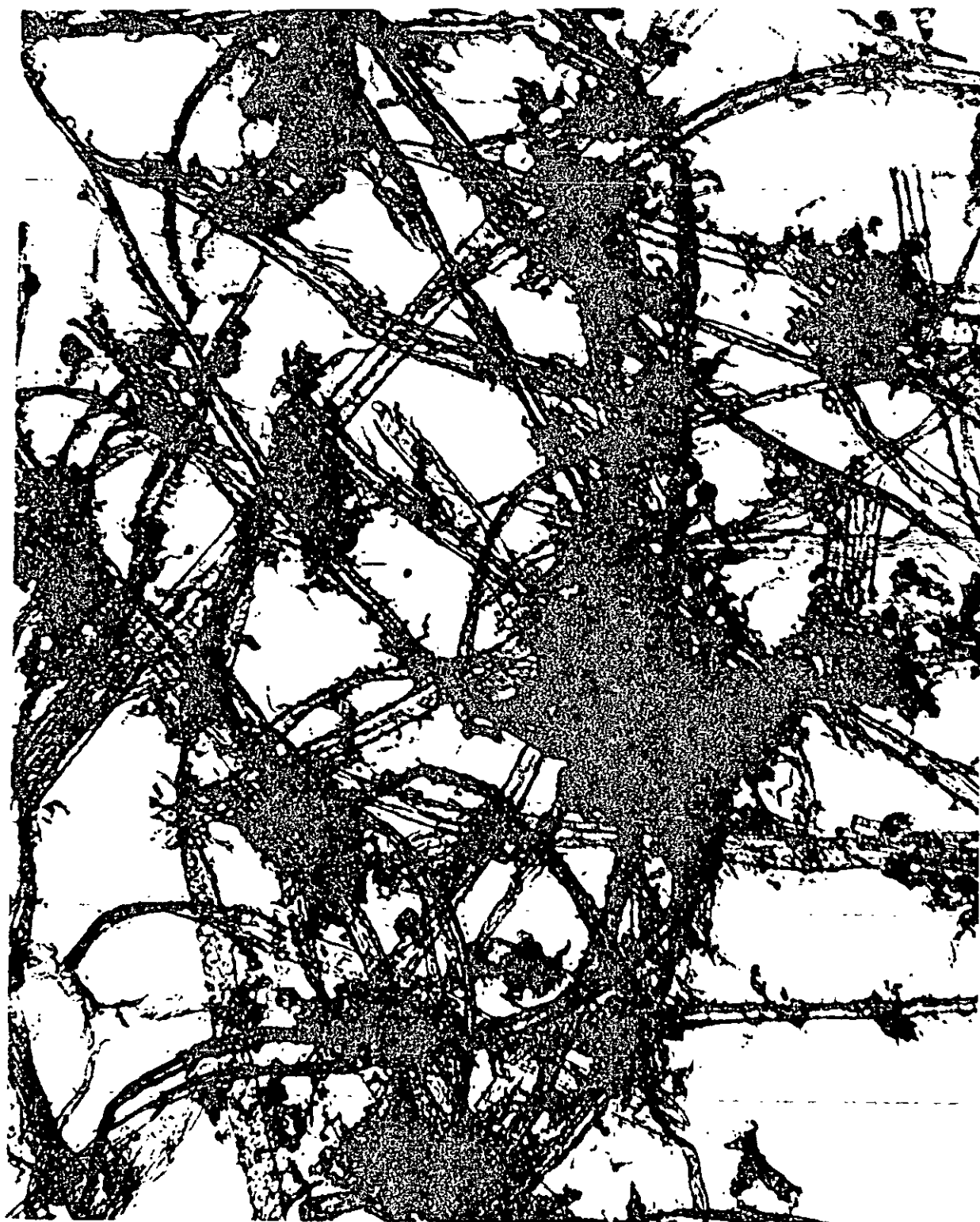


Figure 2
40% Synco 721
60% Bleached Sulfite 368 C.S. freeness
X100



Figure 3.
40% Experimental Resin 751-32
(acid advanced)
60% Bleached Sulfite 368 C.S. freeness
X100