

## Preparation and Properties of Phenolic Resin Laminates. I. Laboratory Evaluation

J. F. MEIER, *Insulation Chemistry, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235*, E. M. BELLOTT, JR., *Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*, and P. P. FRANK, *Westinghouse Oceanic Division Annapolis, Maryland 21404*

### Synopsis

The preparation and properties of sodium carbonate and sodium hydroxide-catalyzed phenolic resins polymerized in 1-liter glass reactors over a broad range of F/P mole ratios are described. Laminates produced from selected sodium carbonate-catalyzed resins coated on kraft paper are discussed and compared with laminates prepared from standard sodium hydroxide-catalyzed resins. Several apparent advantages of the sodium carbonate-catalyzed resin systems over the sodium hydroxide-catalyzed resins are presented. The superior performance is attributed to the high degree of crosslinking resulting from the high concentration of methylolated phenols present in the sodium carbonate-catalyzed resin.

### INTRODUCTION

Phenol-formaldehyde resins are divided into two main classes—novolacs and resoles. Novolacs, named by Baekeland<sup>1</sup> because of their similarity to shellac resins, are almost invariably prepared by heating phenol and formaldehyde with acid catalysis at a formaldehyde-to-phenol (F/P) mole ratio of less than 1. These resins are usually dehydrated and cooled to give glassy products which are pulverized, compounded with fillers, hexamethylenetetramine, flow promoters, etc., and employed as industrial molding powders.

Resoles, on the other hand, are base-catalyzed phenol-formaldehyde resins generally prepared with an F/P mole ratio of greater than 1. Resoles are prepared by refluxing phenol, formaldehyde (usually as a 37% formalin solution), catalyst (most often sodium hydroxide), and water for a variable period of time, resulting in a water- or alcohol-soluble varnish. Water solubility is related to degree of condensation of the phenol and formaldehyde and lower alcohols are often added to attain solubility and/or maintain adequate resin storage stability.

The finished resin is useful for coating or impregnating paper, cloth, glass fabric, etc., which is subsequently used to prepare industrial or decorative laminates. Indeed, an entire industry has developed and is associated with laminating varnishes or resins.

Even though these materials have been of great commercial interest for many years, it was not until the mid-1950's that the reaction mechanisms of phenol-formaldehyde condensations were determined unequivocally. After first syn-

thesizing the various poly(methylol phenols),<sup>2</sup> Freeman employed paper chromatography to determine quantitatively the position and concentration effects of the various methylol phenols.<sup>3</sup> Subsequently, in their classical mechanism paper,<sup>4</sup> Freeman and Lewis employed paper chromatography to follow quantitatively the appearance and disappearance of individual methylol phenols in the phenol—formaldehyde reaction mixture.

Although considerable literature has been published regarding phenol-formaldehyde resins in general,<sup>5</sup> few specific data are presented for phenol-formaldehyde resins prepared as a function of F/P mole ratio, catalyst level, type of catalyst, and reflux times.

It is the purpose of this paper to discuss the properties of the sodium carbonate-catalyzed phenol-formaldehyde resins as a function of F/P mole ratio, and reflux time at a constant  $\text{Na}^+$ /phenol mole ratio. Comparative laminate evaluation data are presented for resoles prepared with sodium hydroxide as the polymerization catalyst.

## EXPERIMENTAL

### Raw Materials

Laboratory-grade fused phenol crystals, laboratory-grade (37% by weight) formaldehyde solution stabilized with 10–15% methanol, and reagent-grade anhydrous sodium carbonate were obtained from the Fisher Scientific Co. and used without further preparation. Sodium hydroxide reagent-grade pellets, obtained from the J. T. Baker Chemical Company, were also used as received.

### Resin Preparations

All laboratory phenolic resin preparations were carried out in 1-liter glass reactors fitted with a stirrer, condenser, thermometer, and entry port. A constant amount of phenol (300 g) and sodium carbonate (3 g) was charged to the resin kettle. The amount of 37% formaldehyde solution was varied between 315 g and 440 g to vary the F/P mole ratio between 1.22 and 1.7. Resin reflux times were varied between  $\frac{1}{2}$  hr and 1 hr for all resins discussed in this paper. The pH was observed to be essentially constant at  $\sim 7.5$  due to the buffering action of excess phenol.

### Determination of Resin Solids and Yield

Per cent solids for each phenolic resin was determined by weighing the amount of residue remaining after a preweighed quantity of resin (1–2 g) was cured for 2 hr at  $130^\circ\text{C}$  on 10 g sand. Based on the per cent solids determination and the theoretical amount of solids anticipated from a known reaction mixture, the yield as a per cent of theory was calculated.

The calculation of the theoretical solids yield for the phenolic reaction mixture is based on two assumptions: (1) The cured phenolic resin contains a negligible quantity of "small" resin molecules, i.e., dimer, trimers, tetramers, etc. (2) The phenyl rings are joined predominantly by methylene-type linkages in the cured resin. In the calculation of the theoretical solids yield, it is, therefore, necessary

to allow for the loss of one molecule of water per molecule of formaldehyde reacted. One way to treat this calculation is to assume that one mole of formaldehyde effectively contributes 12 g to the molecular weight of the cured resin structure, the other 2 g for a  $-\text{CH}_2-$  linkage being allowed for due to loss of H from phenol. The net result is that only 14.8% of the formaldehyde solution contributes to the solids yield.

A sample calculation of theoretical solids yield will serve to illustrate:

Reactant	Amount, lb	Per cent contribution to solids yield, %	Theoretical resin solids, lb
Phenol	3000 lb	100	3000 lb
37% $\text{CH}_2\text{O}$	3150	14.8	466
NaOH	10	57.5	5.75
$\text{H}_2\text{O}$	1230	0	0
$\text{CH}_3\text{OH}$	10	0	0
Total wt.	7400 lb		Total theoretical solids 3471.7 lb

$$\text{Theoretical per cent solids} = \frac{3471.7}{7400} \times 100 = 46.9\%$$

### Determination of Per Cent Formaldehyde

Free or unreacted formaldehyde content of the phenolic resins was determined by the hydroxylamine hydrochloride method.<sup>6</sup> Formaldehyde, present as a hemiformal of the methylol phenols, dissociates and is also titrated as free formaldehyde by this method.

### Per Cent Water Dilutability

The measurement of water dilutability is a method for determining the degree of resin condensation. It is based on the fact that water tolerance decreases as the molecular weight increases. Often, methanol or other low molecular weight alcohols are added to a phenolic resin to dilute to proper paper treating concentrations and/or to give the desired resin storage stability.

Water dilutability is determined by adding water to a premeasured quantity of resin (usually 10 ml) in a graduated cylinder until the resin precipitates. The volume of water added is divided by the volume of sample to obtain the water dilutability value.

The water dilutability of the resins prepared with Fisher laboratory-grade formaldehyde is abnormally high due to the 10–15% methanol content. Usually, formaldehyde for industrial resin manufacture contains less than 1% methanol, and the resulting resins possess considerably lower water dilutability. A subsequent paper will explore the subject of resin dilutability in greater depth.

### Paper Treating

All phenolic resins prepared in the laboratory were hand dipped on kraft paper to a coating ratio of ca. 1.50 and a per cent volatile level of close to 5%. (Ratio = weight of a unit area of resin treated paper/weight of the same unit area of untreated paper, with a specified volatile and greenness level; per cent volatile = per cent weight loss from a 6 in.  $\times$  6 in. sheet of treated paper upon heating 10 min at 302°F.)

### Laminate Preparation

Five in. by 8 in. laminates were plied up using seven phenolic-treated core sheets, one decorative print sheet treated with melamine resin, and one layer of melamine-treated  $\alpha$ -cellulose paper.

Adopted as standard procedure was the simultaneous preparation of two laminates—one using sodium hydroxide-catalyzed phenolic resin and one using sodium carbonate-catalyzed phenolic resin—with a layer of mold release-treated aluminum foil separating the two boards.

A thermocouple was inserted in the middle of the two-board pack to monitor temperature. The laminates were cured for 10 min at 300°F and 1000 psi, cooled to about 100°F, and demolded.

The melamine-treated print and  $\alpha$ -cellulose papers were used as a uniform decorative surface for both sodium carbonate- and sodium hydroxide-catalyzed laminates.

### Laminate Evaluation

After molding, all laminates were cut into pieces  $\sim$  1 in.  $\times$  3 in., weighed, and the thickness measured to the nearest 0.001 in. The individual pieces were boiled in water for a period of 2 hr and the per cent weight gain and thickness increase computed according to NEMA standards.<sup>7</sup>

## RESULTS AND DISCUSSION

### Resin Response Characteristics

Several series of phenolic resins were prepared at various F/P mole ratios using variable reflux time, with sodium carbonate or sodium hydroxide catalyst. Evaluation data for the sodium carbonate-catalyzed resins prepared using a 1-hr reflux time and a  $\frac{1}{2}$ -hr reflux time are presented in Tables I and II, respectively. Data for the sodium hydroxide-catalyzed resins using a 1-hr reflux time are presented in Table III. Included in these three tables are material charge, reflux time, F/P mole ratio, Na<sup>+</sup>/phenol mole ratio, per cent solids, water dilutability, and free formaldehyde content of the resin.

Graphic comparisons of resin yield, water dilutability, and free formaldehyde in the resin as a function of F/P mole ratio, reflux time, and catalyst type are presented in Figures 1–3, respectively. Figure 1 shows that with a 1-hr reflux time, the resin yield obtained from sodium carbonate catalyst is consistently higher than that of the sodium hydroxide catalyst. Sodium carbonate-catalyzed phenolic resin systems refluxed for  $\frac{1}{2}$  hr show a considerably lower resin yield than that obtained with the 1-hr reflux time.

TABLE I  
Phenolic Resin Properties as a Function of F/P Mole Ratio for Sodium Carbonate Catalyst and 1-Hour Reflux

	A	B	C	D	E	F	G	H	I	J	K
Phenol	300	300	300	300	300	300	300	300	300	300	300
CH <sub>2</sub> O (37%)	315	326	335	335	350	360	362	374	388	414	440
Na <sub>2</sub> CO <sub>3</sub>	3	3	3	3	3	3	3	3	3	3	3
F/P Mole ratio	1.22	1.26	1.30	1.30	1.35	1.39	1.40	1.45	1.50	1.60	1.70
Mole Na <sup>+</sup> /mole phenol × 10 <sup>2</sup>	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77
% Solids, theoretical	56.2	55.5	54.5	54.5	54.1	53.4	53.4	52.8	51.8	50.4	48.9
% Solids, experimental	51.9	51.2	51.0	51.6	52.6	50.5	51.3	50.1	50.9	49.4	48.7
% Yield of theory	92.5	92.3	93.5	94.5	97.3	95.7	96	95.5	98.2	98.0	99.5
% Water dilutability	155-160	145	150	170	155-160	150	130-135	180	145-150	145-150	180-185
% Free CH <sub>2</sub> O <sup>a</sup>	1.09	1.30	1.45	1.77	1.82	1.59	2.05	2.25	2.76	2.68	3.91

<sup>a</sup> Hydroxylamine hydrochloride technique.<sup>6</sup>

TABLE II  
Phenolic Resin Properties as a Function of F/P Mole Ratio for Sodium Carbonate Catalyst and 0.5-Hour Reflux

	A <sup>a</sup>	B	C	D	E	F	G	H	I
Phenol	300	300	300	300	300	300	300	300	300
CH <sub>2</sub> O (37%)	315	335	362	372	388	388	414	414	440
Na <sub>2</sub> CO <sub>3</sub>	3	3	3	3	3	3	3	3	3
F/P Mole ratio	1.22	1.30	1.40	1.44	1.50	1.50	1.60	1.60	1.70
Moles Na <sup>+</sup> /moles phenol × 10 <sup>2</sup>	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77	1.77
% Solids, theoretical	56.2	54.5	53.4	52.8	51.8	51.8	49.2	49.2	48.9
% Solids, experimental	45.5	47.1	47.6	42.9	45.4	44.6	46.2	42.0	41.3
% Yield of theory	81.0	86.5	89.1	81.5	87.5	86.5	93.5	85.5	84.5
% Water dilutability	495	380	420	620	510	560	500	615	640
% Free CH <sub>2</sub> O	1.82	2.62	3.33	3.44	4.30	3.59	4.57	4.23	5.18

<sup>a</sup> Resin designation (see Table I).

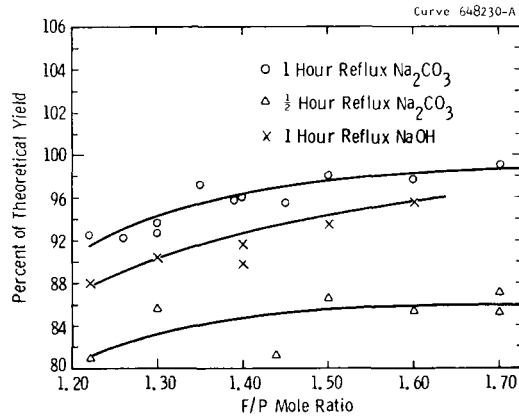


Fig. 1. Per cent theoretical yield as a function of F/P mole ratio for two catalyst systems and two reflux times.

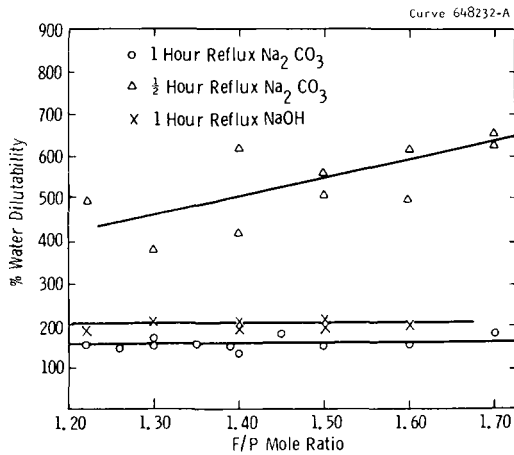


Fig. 2. Per cent water dilutability as a function of F/P mole ratio for two catalyst systems and two reflux times.

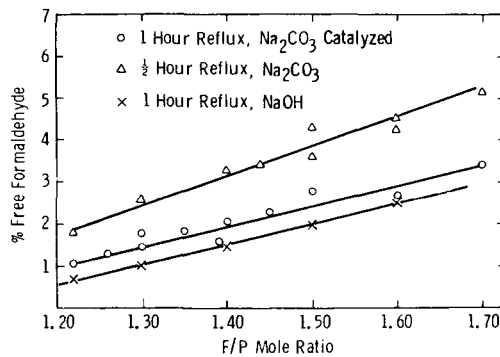


Fig. 3. Per cent free formaldehyde as a function of F/P mole ratio for two catalyst systems and two reflux times.

Resin dilutability data of Figure 2 support the data of Figure 1. The resins prepared with sodium carbonate catalyst at 1 hr of reflux exhibit the least water dilutability (highest degree of condensation). Resins prepared with sodium

TABLE III  
Phenolic Resin Properties as a Function of F/P Mole Ratio for Sodium Hydroxide Catalyst and 1-Hour Reflux

	A	B	C	D	E
Phenol	300	300	300	300	300
CH <sub>2</sub> O (37%)	315	335	362	388	414
NaOH	2.6	2.6	2.6	2.6	2.6
F/P Mole ratio	1.22	1.30	1.40	1.50	1.60
Moles Na <sup>+</sup> /moles phenol × 10 <sup>2</sup>	2.03	2.03	2.03	2.03	2.03
% Solids, theoretical	56.2	54.5	53.4	51.8	49.2
% Solids, experimental	49.5	49.7	49.0	48.5	47.0
% Yield of theory	88.1	91.5	91.7	93.5	95.5
% Water dilutability	185	210	207	195	200
% Free CH <sub>2</sub> O	0.70	1.02	1.48	1.98	2.52

carbonate catalyst and refluxed for ½ hr show the highest water dilutability (lowest degree of condensation). Although the yield curve for the resins prepared with 1 hr of reflux using sodium hydroxide is close to the 1-hr sodium carbonate curve, the water dilutability is slightly higher, since the Na<sup>+</sup>/phenol mole ratio is  $2.0 \times 10^{-2}$  for the sodium hydroxide resin system and somewhat less ( $1.77 \times 10^{-2}$ ) for the sodium carbonate system.

In a similar manner, the per cent free or unreacted formaldehyde present at the end of a resin preparation is plotted as a function of F/P ratio in Figure 3. These data follow the trend established with yield and water dilutability. That is, the free formaldehyde content for the 1-hr reflux with sodium carbonate is slightly less than that found for the ½-hr reflux with carbonate and slightly greater than that found for 1 hr of reflux with the hydroxide system.

### Paper Treating

Only the sodium carbonate-catalyzed experimental resins shown in Table I were hand dipped on kraft paper after dilution to ~30% solids with water. Resin coating parameters are shown in Table IV. Considerable difficulty was encountered in controlling the ratios with the water-dilutable resin systems, and drying to the desired volatile content took two to three times as long as the alcohol-diluted control resin.

### Laboratory Laminate Evaluation

The per cent weight gain and thickness increase data for the laminates prepared from various resins are summarized in Table V. The paper-treating ratio for the sodium carbonate-catalyzed laminates is somewhat higher than that of the sodium hydroxide-catalyzed laminates. However, in the one case where a paper treating ratio of 1.40 was attained for sodium carbonate-catalyzed laminate, the weight gain and thickness increase of the carbonate-catalyzed laminate were lower than those of the sodium hydroxide-catalyzed laminate. Water boil data, graphically presented in Figures 4 and 5, contrast the response for sodium hydroxide- and sodium carbonate-catalyzed laminates and clearly demonstrate the superiority of resins prepared with sodium carbonate catalyst.



TABLE IV  
Paper Treating Parameters

	A <sup>a</sup>	B	C	D	E	F	G	H	I	J	K	
F/P	1.22	1.26	1.30	1.30	1.35	1.39	1.40	1.40	1.45	1.50	1.60	1.70
Paper treating ratio	1.57	1.56	1.55	1.55	1.50	1.57	1.53	1.40	1.56	1.56	1.49	1.52
% Volatile	4.80	5.05	5.17	5.00	5.27	6.90	5.93	5.40	3.90	4.10	6.35	6.50

<sup>a</sup> Resin designation (see Table I).

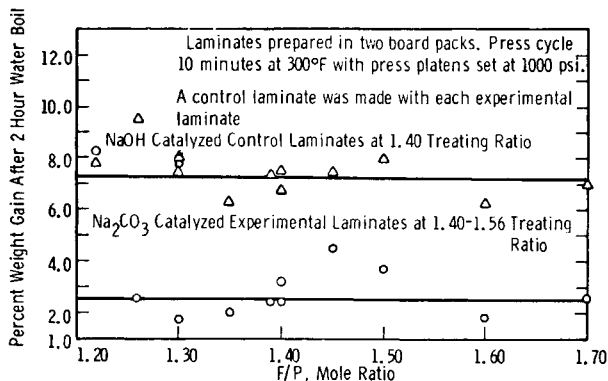


Fig. 4. Per cent weight gain vs. formaldehyde:phenol mole ratio for laminates prepared from sodium carbonate-catalyzed phenolic resin.

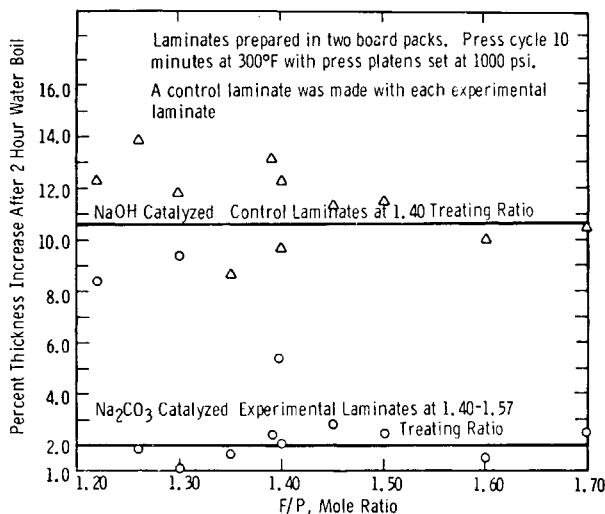


Fig. 5. Per cent thickness increase vs. formaldehyde:phenol mole ratio for laminates prepared from sodium carbonate-catalyzed phenolic resin.

## CONCLUSIONS

A series of sodium carbonate-catalyzed phenolic resins with formaldehyde/phenol mole ratios of 1.22 to 1.7 were prepared at reflux times of 1 hr and  $\frac{1}{2}$  hr and compared with resins employing sodium hydroxide as catalyst. For the sodium carbonate system and a 1-hr reflux time, the resin yield varies significantly over the range F/P 1.22-1.7, increasing from ca. 92% to 98% of theory. Yield values are generally  $\sim 5\%$  lower for a similarly prepared resin using a sodium hydroxide catalyst.

Water dilutability of the resins prepared with sodium carbonate and 1 hr of reflux is slightly lower than for similarly prepared resins using sodium hydroxide as catalyst, suggesting lower molecular weight in the latter case.

TABLE V  
Summary of Water Boil Data<sup>a</sup> for Experimental and Control<sup>b</sup> Laminates

Resin designation (Table I)	Paper treating ratio	% Wt gain <sup>c</sup>	% Thickness increase <sup>c</sup>
A <sup>d</sup>	1.57	8.3	8.4
Control <sup>b</sup>	1.40	7.9	12.3
B	1.56	2.60	1.87
Control	1.40	9.50	13.9
C	1.55	1.74	1.12
Control	1.40	7.43	15.7
D	1.55	7.8	9.4
Control	1.40	8.0	11.0
E	1.57	1.98	1.66
Control	1.40	6.25	8.70
F	1.57	2.41	2.42
Control	1.40	7.33	17.91
G	1.53	2.42	2.01
Control	1.40	6.78	9.69
G	1.40	3.26	5.34
Control	1.40	7.41	12.30
I	1.56	3.7	2.42
Control	1.40	7.9	11.5
H	1.56	4.5	2.88
Control	1.40	7.4	11.3
J	1.49	1.82	1.51
Control	1.40	6.18	10.01
K	1.52	2.55	2.51
Control	1.40	7.00	10.50

<sup>a</sup> All experimental resins coated on kraft paper as shown in Table IV. All cure cycles 10 min at 300° F with press platens set at 1000 psi.

<sup>b</sup> Kraft paper, print paper, and overlay paper coated with appropriate resins were prepared in bulk to serve as a control for this experiment.

<sup>c</sup> Average of three determinations.

<sup>d</sup> Resin designation (see Table I).

Laminates prepared from sodium carbonate-catalyzed phenolic resin-treated paper exhibit less than one third the weight gain and thickness increase of the sodium hydroxide-catalyzed specimens after 2 hr of water boil.<sup>8</sup> However, an optimum F/P mole ratio has not been defined for the sodium carbonate-catalyzed resin system.

The authors wish to acknowledge the assistance of Dr. J. H. Freeman for his helpful discussions, suggestions, and encouragement throughout this work, and for his review of the manuscript.

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Received January 9, 1976

Revised February 6, 1976