

The Chemistry of Fast-Curing Phenolic Adhesives. II

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Synopsis

Novolak-like materials have been prepared by reaction of phenol-formaldehyde resoles with aromatic amines. The hydroxymethyl groups present in resoles react with the ring carbons and the amino groups of the aromatic amine. Proportions of the two types of product vary with the amine used.

INTRODUCTION

Phenolic resins, made by the acid- or base-catalyzed condensations of phenols with formaldehyde, are well known and have been described at length many times.¹ The previous paper in this series reports the formation of extremely useful materials from the reaction of phenolic resoles with amines.² The present paper will examine the formation, structures, and chemical reactions of those amine-modified phenolic resins.

EXPERIMENTAL

Preparation and Screening Techniques

Resole Preparation. A mixture of 42.06 parts of 100% phenol, 11.35 parts of 91.0% paraformaldehyde flake, 4.51 parts of water, and 0.46 parts of calcium acetate was prepared at 25°C. The mixture was brought to reflux (109°C) in 60 min at a uniform rate, held at reflux for 120 min, cooled, and stored. This material will usually be referred to as "phenolic prepolymer A."

Although the mole ratio of formaldehyde to phenol (0.77) used in preparation suggested that prepolymer A should be a novolak, prepolymer A was actually a mixture of resole, which possessed the hydroxymethyl absorption at 10.0 microns typical of resoles,³ and some unreacted phenol.

Preparation of Amine-Modified Novolaks. A mixture of 100 g prepolymer A and 0.305 mole amine (or other modifying agent) was refluxed for 2.25 hr and cooled, and 26.3 g methanol was stirred in to prevent phase separation.

Separation of Resins for Characterization of the Isolated Polymeric Fractions. Resins were prepared as above from prepolymer A and selected modifying agents. The resins, including prepolymer A above, were each extracted with hot water until no more organic material would enter the aqueous phase. The polymeric residues were then lyophilized to give dry, thermoplastic solids of very low melting point. In some cases, these resin fractions were dissolved in methanol, cured with methyl formcel, ground to 80 mesh, and washed with methanol.

Analytical Techniques

Amine Content of Modified Polymers. Total amine was determined by potentiometric titration with 0.1*N* HCl in a 1:1 ethylene glycol-isopropyl alcohol mixture. Primary amine was determined by the method of Hawkins et al.⁴ Tertiary amine was titrated potentiometrically in 1:1 ethylene glycol-isopropyl alcohol solution after acetylation of the mixture with acetic anhydride.

Residual *m*-Hydroxylaniline and *m*-Phenylenediamine in Amine-Modified Resins. Amine-modified resin samples were solvent transferred into dry pyridine, silylated with *N,O*-bistrimethylsilylacetamide, followed by gas chromatography on 5% SF 96 on Haloport F at 170°C. The internal standard used was 1,3,5-tribromophenol.

Characterization of Isolated Resin Fractions

Stroke Cure. The water-extracted, lyophilized prepolymers modified with *m*-hydroxylaniline (MHA) or *m*-phenylenediamine (MPD) were placed on a hot plate at 150°C. They remained liquid for 10 min and showed no sign of hardening. On addition of paraformaldehyde, they cured immediately to solids insoluble in 1:1 acetone-water.

Gel Time and Cross-Lap Strength. Samples of isolated, amine-modified resins made from MHA and MPD were dissolved in warm *N,N*-dimethylformamide (2 parts resin to 1 part solvent). One part hardener was then mixed with 2 parts of this isolated resin solution and spread on a wooden block. A second block was placed over the first to make a contact area of 1 sq in., and a pressure of 40 psi was applied for 12 min. The tensile force per unit area necessary to separate the blocks was then found to be 235 psi for the MHA-modified resin and 275 psi (gel time 55 sec) for the MPD-modified resin.

Amine Content of Isolated Resin Fractions. Samples of isolated MHA- and MPD-modified resins were titrated for amine content by the usual procedures. Secondary-amine content was inferred by difference. Free monomeric amine was determined by gas chromatography. Total nitrogen was also measured by combustion. Results appear in Tables II and IV. Isolated resin fractions cured with methyl formcel could not be titrated for amine content, apparently because the ground, cured resin was insoluble in the titration medium.

TABLE I
Reaction of Amines and Resorcinol with *o*-Hydroxybenzyl Alcohol

Reagent	Extent of reaction, ^a %		Major product			Minor product		
			Mole ratio A/B ^b	% Yield ^c	MW ^d	Mole ratio A/B ^b	% Yield ^c	MD ^d
Aniline	20	25	1/1	21%	199	1/2	1.0	305
Methylene-dianiline	20	20	1/1	15	304	1/2	5%	410
<i>m</i> -Hydroxyaniline	100	100	1/1	90	215	1/2	5%	321
Resorcinol	100	100	1/1	90	216	1/3	5%	427
						1/2	5%	322
						1/3	5%	428

^a Based on *o*-hydroxybenzyl alcohol reacted; IR = infrared; PMR = proton magnetic resonance.

^b Mole ratio of amine or resorcinol (A) to *o*-hydroxybenzyl alcohol (B), as indicated by gel permeation-chromatographic molecular weight.

^c Based on areas of the appropriate GPC peaks and the amount of *o*-hydroxybenzyl alcohol reacted.

^d Gel permeation chromatographic data using novolak calibration on Styragel in tetrahydrofuran.

Spectroscopic and Molecular Weight Measurements on the Isolated Resin Fractions. Proton magnetic resonance and gel permeation-chromatographic analyses and interpretations were performed on the isolated resin fractions by personnel of the analytical laboratories at Dow Chemical Co., Midland, Michigan. Proton magnetic resonance spectra were obtained in deuterated dimethyl sulfoxide, and the gel permeation chromatograms were run on a 14-ft Styragel (10^4 Å) column in tetrahydrofuran, using a Waters apparatus. Molecular weights were occasionally cross-checked by ebulloscopic measurement.

Spot Tests for Secondary Amine in the Reaction Product of *m*-Hydroxyaniline with Formaldehyde. Two spot tests⁵ were performed to detect the presence of secondary amine in the isolated, modified resin fraction. Both the dithiocarbonic acid and the nitroprusside tests indicated the presence only of traces of secondary amine.

Reaction of Modifying Agents with Benzyl Alcohol and *o*-Hydroxybenzyl Alcohol. To 0.136 mole of either benzyl alcohol or *o*-hydroxybenzyl alcohol, 4.5 g water, and 0.46 g calcium acetate, 0.305 mole modifying agent was added. Modifying agents used were aniline, methylenedianiline, *m*-hydroxyaniline, and resorcinol. The resulting mixtures were heated at 100°C for 2¹/₄ hr. The products were then analyzed by infrared analysis, proton magnetic resonance, and gel permeation chromatography. Where desirable, the major product was isolated and analyzed separately. In all of the reactions utilizing benzyl alcohol, there was essentially no product formed. With *o*-hydroxybenzyl alcohol, however, reactions occurred in each case. The results are given in Table I.

Components of the *m*-aminophenol and resorcinol model systems could be fractionated by their H₂O solubility. The 1:2 and 1:3 adducts were insoluble in hot water, while the remainder were soluble. Thorough extraction isolated the hot water-insoluble, tarry materials from the remainder of the reaction mixtures. On cooling of the hot-water extracts, the 1:1 adduct precipitated in an almost pure state as indicated by gel permeation chromatography. The 1:1 *o*-hydroxybenzyl alcohol-*m*-aminophenol adduct melted 155–185°C while the resorcinol analogue melted 183–187°C. The remaining materials, soluble in cold water, were unreacted *m*-aminophenol or resorcinol. The aniline system could be treated in a similar fashion, but the methylenedianiline system was intractable.

RESULTS AND DISCUSSION

Resin Modification

A brief study of uptake of modifying agents by prepolymer A as a function of time at reflux was performed. The indicated amounts of *m*-hydroxyaniline or resorcinol and prepolymer A were mixed and brought to reflux (105°C) as rapidly as possible. Aliquots were taken at intervals and freeze dried, and residual modifier was determined by gas chromatography. Figure 1 presents uptake of each modifier separately. Zero time was plotted as the point at which the system reached reflux. Resorcinol and *m*-hydroxyaniline uptakes as a function of time were comparable. However, Figure 2 demonstrates that *m*-hydroxyaniline competed very effectively with resorcinol for the actual sites on prepolymer A, because it

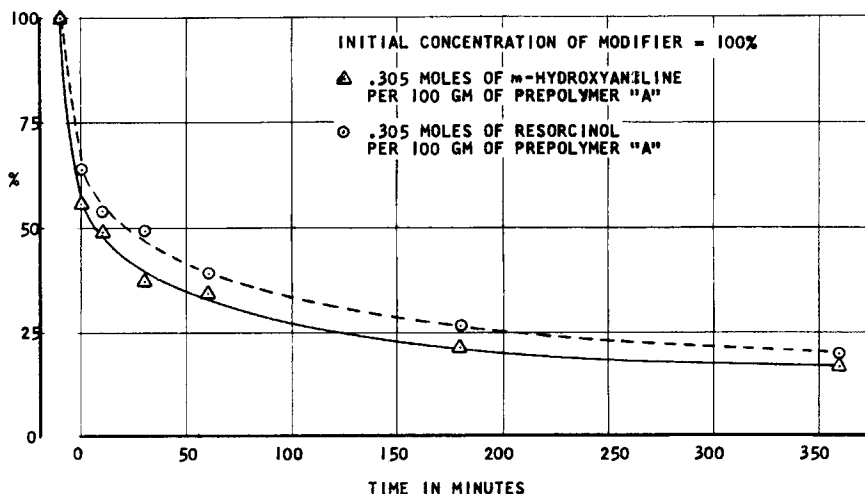


Fig. 1. Uptake of *m*-hydroxyaniline and resorcinol by prepolymer A as function of time at reflux. Residual modifier, separate.

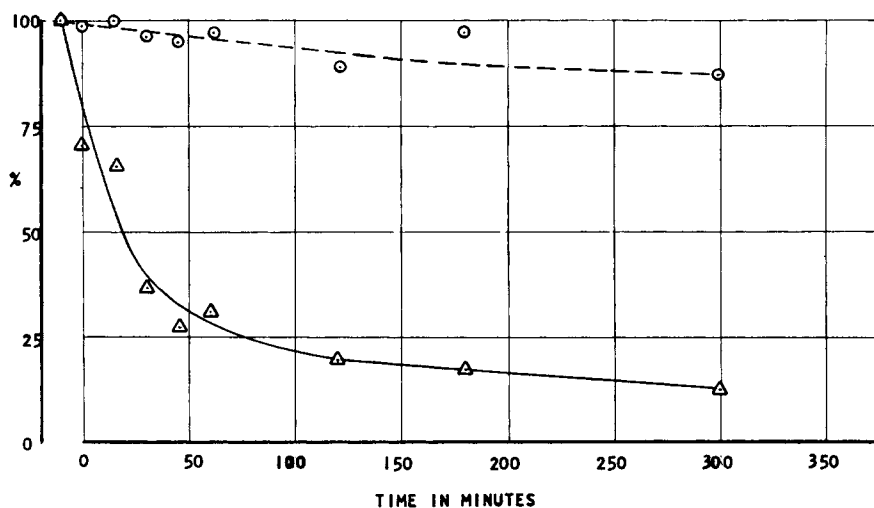


Fig. 2. Uptake of *m*-hydroxyaniline and resorcinol by prepolymer A as a function of time at reflux. Residual modifier, mixed. Symbols same as in Fig. 1.

was about 90% reacted with prepolymer A, and resorcinol only 10% reacted when the two modifiers were placed in competition for prepolymer A.

Model Systems

The amine-modified prepolymer A system was studied, using benzyl alcohol and *o*-hydroxybenzyl alcohol as models for the resole and aniline, methylenedianiline, *m*-hydroxyaniline, and resorcinol as modifying agents.

The data on the model systems, Table I, indicate that the monosubstituted aniline and the *p*-disubstituted methylenedianiline react quite differently from the *m*-disubstituted *m*-aminophenol and resorcinol. While the latter two reacted with all the *o*-hydroxybenzyl alcohol present, the two aniline derivatives only reacted with 20% of it in the 2¹/₄-hour reaction period.

In addition, the two *m*-substituted materials not only gave the 1:1 adduct with *o*-hydroxybenzyl alcohol as the major product but produced some 1:2 and 1:3 adducts. The aniline and methylenedianiline only had 1:1 and 1:2 adducts. It was of interest that although methylenedianiline was not too reactive, it tended to have a greater preference toward formation of the 1:2 adduct (25% of the total product) than the other materials (5% of the products). The *m*-substituted materials, however, were the only ones to form 1:3 adducts. This indicates that, depending on the ratio of meta compound to free $-\text{CH}_2\text{OH}$ groups, the meta compound (*m*-aminophenol or resorcinol) will cap off the free $-\text{CH}_2\text{OH}$ groups at the high ratios of modifier to *o*-hydroxybenzyl alcohol used in the model studies, or will act as a nucleus for molecular weight buildup by becoming polysubstituted at the low ratios of modifier to hydroxymethyl compound used in amine-modified resins having 0.2 mole aryl amine/100 g prepolymer A.

Structure of Modified Prepolymers

Modified and unmodified prepolymers were isolated by washing with large quantities of hot water. This treatment removed unreacted monomeric amine and some phenol, as well as catalyst and other water-soluble materials. The residues were then freeze dried. In a stroke-cure test, samples of the acetone-soluble, amine-modified prepolymer were found to melt reversibly at 150°C. Addition of a little formaldehyde donor such as paraformaldehyde to the melt caused immediate hardening to a permanently infusible, acetone-insoluble material. This is the usual behavior of novolak-type resins.

Prepolymer A was modified with various quantities of *m*-hydroxyaniline or aniline at several amine concentrations. The amine novolaks and the resole fraction of prepolymer A were then isolated by washing with hot water, followed by freeze drying. Molecular weight measurements and nitrogen contents of these polymers are listed in Table II.

The amine content of the resin was determined from its nitrogen content. Essentially, the same amine content values could be obtained from the proton magnetic resonance data for *m*-aminophenol and *m*-phenylenediamine, where hydrogens characteristic of these structures could be observed. Both the type of modifying amine and the amount of the amine present had an effect on molecular weight of the isolated fractions, as shown in Table II. All the amines studied raised the average molecular weight of the unmodified prepolymer A resin by a factor of 3 or more. Of the amines, at equivalent amine content, *m*-phenylenediamine produced the greatest increase in molecular weight, followed closely by *m*-aminophenol,

TABLE II
Molecular Weights and Nitrogen Contents of the Amine-Modified Prepolymer A

Resin no.	Amine	Amine charged ^a	\bar{M}_n^b	\bar{M}_n^c	% N	Amine found ^a
1	none	0	225	—	0	0
2	<i>m</i> -hydroxyaniline	—	650	680	4.26	0.456
3	<i>m</i> -hydroxyaniline	0.305	800	—	—	0.29
4	<i>m</i> -hydroxyaniline	0.229	1100	1100	2.44	0.215
5	<i>m</i> -hydroxyaniline	0.127	1250	insoluble	1.56	0.127
			(partly insoluble)			
6	<i>m</i> -phenylenediamine	0.305	940	—	—	0.30
7	aniline	0.220	650	640	3.33	0.305
8	aniline	0.129	700	730	2.81	0.247
9	aniline ^d	0.220	650	670	4.22	0.418
10	aniline ^d	0.129	900	910	3.34	0.305

^a Moles of amine per 100 g prepolymer A.

^b Number-average molecular weight determined using the GPC curve maximum and a novolak calibration.

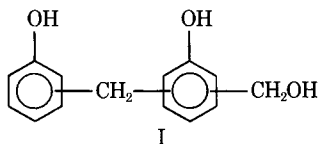
^c Number-average molecular weight determined by ebullioscopy.

^d pH adjusted to 4.5 near middle of cook.

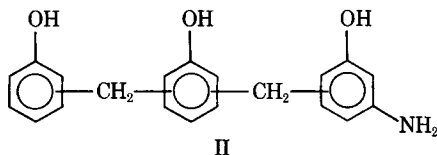
then aniline·HCl, and finally aniline. For a given amine, at different amine contents, the molecular weight increased with decreasing amine content. This effect was more pronounced with *m*-aminophenol than with aniline.

The *m*-hydroxyaniline-modified resins listed in Table II had amine contents (based on nitrogen analysis) similar to the amount of amine charged to the reaction vessel during prepolymer modification. With aniline, all amine contents of isolated resins were higher than the amount charged. This ranged from a low of 1.5 times for aniline cooks to 3.5 times for aniline·HCl cooks. The only explanation at the present time for this increase in aniline content is that these cooks bound in all available aniline rather than some water-soluble portions of prepolymer A. The unbound, water-soluble parts of prepolymer A were then lost during water extraction. In the case of *m*-hydroxyaniline, most of the amine and essentially all the prepolymer A were converted to materials insoluble in water. In the latter case, gel permeation chromatography has shown that, while all the free *m*-hydroxyaniline was extracted with hot water, only ~40% of the free phenol was extracted, despite its solubility in water.

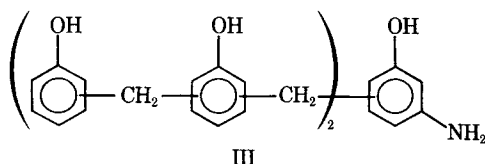
The molecular weights of the isolated resin fractions listed in Table II increased with *decreasing* amine content. This can be rationalized as follows. The initial resole fraction of $\bar{M}_n \sim 225$ contained, on the average, no more than two phenol units and might be represented as compound I



molecular weight = 230): although larger fragments were undoubtedly present. No evidence of smaller fragments appeared in the gel permeation chromatograms. At higher amine concentrations, reactions of amine with I would tend to give 1:1 adducts II (molecular weight = 321);



However, as amine concentration declined, relative concentration of I would increase and adducts would approach a ratio of resole:amine of 2:1 or higher (III, molecular weight = 533):



Crosslinking via arylamine units would also become more common at

TABLE III
Gel Time (Curing Speed) of Amine-Modified Novolaks as a Function
of Amine Content and \bar{M}_n

Prepolymer A modified with	Moles amine per 100 g prepolymer A	\bar{M}_n^a	Gel time, sec	pH
<i>m</i> -Hydroxyaniline	0.305	800	30	3.5
	0.229	1100	—	—
	0.153	—	15	3.5
	0.127	> 1250	—	—
	0.078	(> 1250) ^b	(0) ^b	—
Aniline	0.305	—	(> 24 hr)	4
	0.22	650	900	4
	0.13	900	240	4
	0.057	—	300	4

^a Number-average molecular weight determined by gel permeation chromatography on isolated polymer.

^b Mixture gelled during preparation of amine-modified novolak.

low amine concentration (IV, molecular weight = 654):

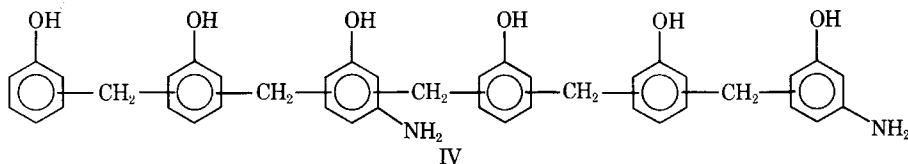
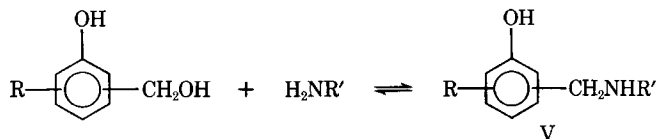


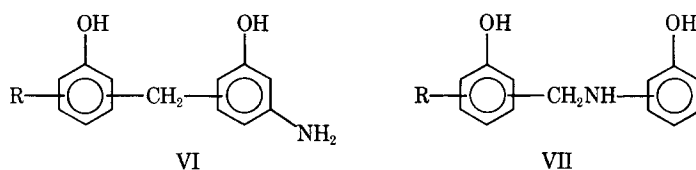
Table III lists curing speed of modified novolaks versus amine content and some molecular weights of the modified novolaks. In the presence of formaldehyde, the modified novolak of lower amine content cured faster than the modified novolak of higher amine content.

Assuming that formaldehyde curing agent reacts at comparable rates with the functional groups in modified novolaks of differing molecular weights, the increase of curing speed with decreasing amine content was simply a reflection of the fact that the higher molecular weight system of lower amine content was poised closer to its gel point.

An aliphatic amine must necessarily be bound to phenolic via a somewhat liable, benzylic carbon-nitrogen bond (V):



m-Hydroxyaniline has the additional possibility of being bound to phenolic by a carbon-carbon bond to the aromatic ring of the amine (VI) or by a carbon-nitrogen bond (VIII):



Case VI should confer stability comparable to an ordinary phenolic resin upon the amine-modified phenolic resin.

The nature of the chemical linkage between the phenolic portion and *m*-hydroxyaniline in modified novolaks was examined by titration, spot tests, and proton magnetic resonance spectra. The presence of large amounts of primary amine groups in the modified novolak would imply carbon-carbon bonding of phenolic to the ring of the aromatic amine as in VI. The presence of secondary and tertiary amino groups would imply carbon-nitrogen bonding as in VII.

Table IV lists the wt-% of arylamino units in isolated, amine-modified novolak. No tertiary amine was detected by titration. Primary amine groups constituted no less than 80% of the total titratable amine. The remaining 10–20% of amine is presumed to be secondary. Spot tests showed very little secondary amine present in the reaction product of *m*-hydroxyaniline with 0.3 equivalents of formaldehyde. The large per cent of primary amine groups and relative lack of secondary and tertiary amine groups imply that most of the resole reacted with the amine ring to form carbon-carbon bonds in the amine-modified novolak. This conclusion may be supported by the fact that nearly the same amount of either *m*-hydroxyaniline or *m*-phenylenediamine molecules were bonded to phenolic fragments in the modified novolak. *m*-Phenylenediamine has the same number of ring bonding sites but twice as many nitrogen bonding sites as *m*-hydroxyaniline.

The proton magnetic resonance (PMR) studies of isolated, amine-modified novolaks listed in Tables V, VI, and VII provide additional structural detail for these novolaks. In Table V are listed the relative quantities of various types of protons distinguished by PMR. Amine contents of resins in Table V may be obtained from Table I.

TABLE IV
Arylamino Units (wt-%) in Isolated, Amine-Modified Prepolymer A Novolak

Amine	Total amine units, wt-%		Aryl units, wt-%, containing		
	By titration	By combustion	—NH ₂	—NHR	—NR ₂
<i>m</i> -Phenylenediamine	25.0 ± 0.6	26.2	22.5	<3.7	0
<i>m</i> -Hydroxyaniline	27.7 ± 0.2	30.4	24.8	<5.6	0
	—	—	24.4	—	—
	—	—	28.0	—	—

The absorptions were normalized to give a total benzylic CH_2 of 2.0. The data are somewhat crude, since some NH and methylol OH could be present (most of the OH and NH protons were replaced by deuterium exchange with the solvent). Aniline caused considerably more secondary amine linkages in the isolated resins than did *m*-hydroxyaniline and *m*-phenylenediamine. In addition, $-\text{CH}_2\text{OCH}_2-$ linkages appeared to be increasing with decreasing MHA content.

Using the PMR data, the composition of the ortho resin, and the amine content, it was possible to determine the types of structures present and roughly the molar proportions of each species present based on a total of

TABLE V
PMR Data on Amine-Modified Novolaks in Deuterated Dimethyl Sulfoxide

Resin no.	Amine	ArH/- ArCH ₂	ArH* ^a / ArH ^a	Ar- CH ₂ Ar	ArCH ₂ - NHAr	ArCH ₂ - OR ^b
1	prepolymer A	3.27/2	—	0.85 0.06	0 ArCH ₂ OAr	1.08
2	<i>m</i> -hydroxyaniline (45%)	4.65/2	0.65/4.00	1.63	0.16	0.19
3	<i>m</i> -hydroxyaniline (29%)	4.04/2	0.82/3.22	1.68	0.12	0.20
4	<i>m</i> -hydroxyaniline (22%)	3.50/2	0.25/3.25	1.35	0.15	0.50
5	<i>m</i> -hydroxyaniline (13%)	2.58/2	0.10/2.48	1.26	0.10	0.63
6	<i>m</i> -phenylene- diamine (30%)	3.63/2	0.13/3.50	1.63	0.09	0.29
7	aniline (31%)	3.93/2		1.04	0.42	0.54
8	aniline (25%)	4.15/2		1.14	0.38	0.48
9	aniline·HCl (42%)	4.75/2		1.25	0.50	0.25
10	aniline·HCl (30%)	2.94/2		1.36	≤0.39	>0.25

^a ArH* = Aryl hydrogens ortho or para to two amino groups or one amino and one hydroxy group. Indicative of the amount of amine present and its extent of substitution.

^b R = H or CH₂Ar.

1 mole of CH₂ groups of all types. These data are given in Table VI for the *m*-aminophenol and *m*-phenylenediamine resins and in Table VII for the aniline resins.

In general, the degree of substitution and the quantity of more highly substituted species increased with decreasing aniline content in agreement with the molecular weight data. Although all the samples, including the isolated prepolymer A, were hot water extracted, some free phenol was present in each. Consequently, the amount found in the hot water-extracted prepolymer A was carried through the other materials for purposes of calculation. It is conceivable that some of the free phenol could

TABLE VI
Probable Structures in Base and Amine Resins


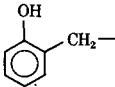
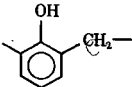
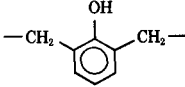
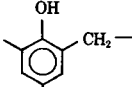
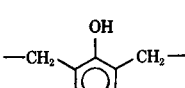
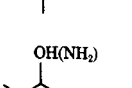
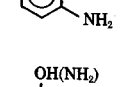
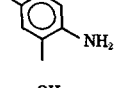
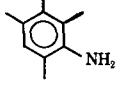
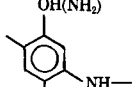

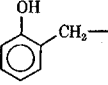
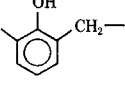
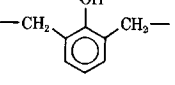
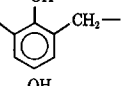
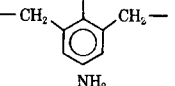







Structure	Resin					
	1 Prepolymer A	2 (45% MHA)	3 (29% MHA)	4 (22% MHA)	5 (13% MHA)	6 (30% MPD)
	0.10	0.10	0.10	0.10	0.10	0.10
	0.43	0.53	0.06	0.25	—	0.42
	0.13	0.07	0.62	0.25	0.23	0.13
	0.22	0.20	0.07	0.25	0.11	0.20
	—	—	—	—	0.27	—
	—	—	—	—	0.14	—
	—	—	0.35	—	—	—
	—	0.41	—	0.175	0.05	0.085
	—	—	—	—	0.04	—
	—	0.08	0.06	—	—	—
	—	—	—	0.075	—	0.045

TABLE VII
 Probable Structures in Aniline Resins

Structure	Resin					10 (30% Aniline· HCl)
	1 Pre- polymer A	7 (31% Aniline)	8 (25% Aniline)	9 (42% Aniline·HCl)		
				(A)	(B)	
	0.10	0.10	0.10	0.10	0.10	0.10
	0.43	0.16	0.32	0.16	0.37	—
	0.13	0.34	0.18	0.34	0.13	0.185
	0.22	0.25	0.25	0.25	0.25	0.135
	—	—	—	—	—	0.365
	—	—	—	—	—	0.125
	—	—	0.08	0.21	—	—
	—	0.13	—	—	0.21	—
	—	—	—	—	—	0.09
	—	—	—	—	—	—
	—	—	0.19	0.25	0.25	—
	—	0.21	—	—	—	—
	—	—	—	—	—	0.25

react during the cooking in of the aniline; but since it is present in a small amount and probably the least reactive species present, it is likely that little would react.

What was also of interest was the increase in substitution on the amines with decreasing amine content. At 25–30% *m*-hydroxyaniline, most of the aniline was mono- or disubstituted. At 10–20%, it was di- and tri-substituted. The *m*-phenylenediamine at ~25% amine content was much like *m*-hydroxyaniline at 11–20%, in agreement with the data presented in Table II.

Aniline, however, was again different. As the data in Table VII indicate, aniline was more heavily substituted on the nitrogen compared to *m*-hydroxyaniline, 50–75% compared to 0–20%. In addition, while lower amine levels led to higher amine substitution with *m*-hydroxyaniline, it did not lead to higher substitution in the aniline or phenolic portion in the aniline cooks, except for the aniline hydrochloride cooks (9 and 10). The aniline cook with 10% aniline (8) was very much like the isolated prepolymer A in phenolic substitution and had mono- and disubstituted amine, whereas the 20% aniline cook (7) was more highly substituted. This would imply greater benzyl ether coupling in aniline 8 than in aniline 7, which could increase molecular weight without increasing substitution.

The odd behavior of the degree of substitution versus amine content found in the aniline 7 and 8 cooks was eliminated in aniline cooks 9 and 10. In the latter two cooks, the pH was lowered so that essentially a 50–50 mixture of aniline and aniline hydrochloride was present. The lower pH did not seem to affect the amount of N substitution versus ring substitution. The ratios were similar under both conditions of reaction.

SUMMARY

Formaldehyde condensation resins with resole-like reactivity may be chemically modified with amines or other formaldehyde-reactive species to produce low molecular weight novolak-like resins. These novolaks may then be cured rapidly, at ambient conditions, on addition of a formaldehyde donor. If phenol-formaldehyde resole is modified with an arylamine, the final cured product is similar in structure to a cured phenolic with some phenol units replaced by arylamine units. The arylamine units are linked to the lattice by both C–C and C–N bonds. Properties of the cured resins are similar to those of ordinary phenolics.

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