N-Methylaniline Formaldehyde: Its Synthesis and Use as an Epoxy Curing Agent

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Synopsis

A series of poly-secondary aromatic amines was prepared by the acid-catalyzed condensation of N-methylaniline with formaldehyde. These condensation products were evaluated as curing agents for a standard epoxy prepolymer, namely bis(2,3-epoxypropoxyphenyl)propane. Various molar ratios of N-methylaniline to formaldehyde were used to produce polyamine condensation products with varying degrees of polymerization. These molar ratios ranged from 1.60 to 1.30. Dielectric properties of the cured epoxy resins at temperatures above 100°C. were highly dependent upon these ratios. Lower-ratio condensation products produced resins with optimum dielectric properties at the higher temperature and also with good physical properties.

BACKGROUND

Epoxy resins were first introduced as thermosetting polymers in the early 1950's. The most commonly used resins in this class are those derived from bisphenol A and epichlorohydrin and are commonly known as diglycidyl ethers of bisphenol A. These resins and the various other epoxy resins are commonly cured by polyfunctional aliphatic amines such as diethylenetriamine, aromatic amines such as *m*-phenylenediamine, 4,4'-diaminodiphenylmethane or 4,4'-diaminodiphenylsulfone, and anhydrides such as phthalic anhydride and methyl nadic anhydride.

Aromatic amine curing agents have been of two types. These include polyfunctional primary amines and tertiary amines. Whereas the former act as chain extenders and become part of the cured polymer molecules, the latter serve as catalysts only and produce polyether resins free from bonded amine moieties.

In the course of a polymerization the primary amines are converted to secondary and, ultimately, to tertiary amines; however, the alkyl groups added during the polymerization are very large moieties and, consequently, steric effects can be quite pronounced.

It was thus the objective of the work presented herein to study secondary aromatic amine curing agents. To accomplish this objective, polyfunctional secondary amines were required. One series of such amines was obtained by the condensation of N-methylaniline with formaldehyde, and their preparation and properties are discussed below.

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DISCUSSION

N-Methylaniline formaldehyde is a condensation product obtained from the acid-catalyzed reaction of *N*-methylaniline with formaldehyde. The material has been found to be an excellent curing agent for epoxy resins. Its preparation may be illustrated in the following general form:
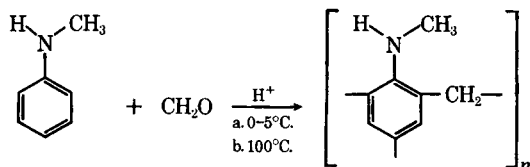
The first of these syntheses utilized 2 moles of the aromatic amine and 1 mole of formaldehyde and may be illustrated as follows:
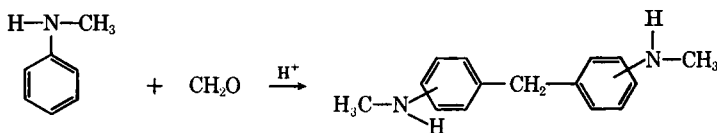
Instead of producing a single compound, the reaction yields a mixture of isomers, which include 4,4'-bis(methylamino)diphenylmethane, 2,2'-bis-(methylamino)diphenylmethane, and 2,4'-bis(methylamino)diphenylmethane, besides a small amount of high telomers. To some extent the various isomers can be separated by molecular distillation at 10^{-3} torr and temperatures of 80–150°C. That portion which distils at the lower temperature tends to crystallize more readily than the higher-boiling portion and thus is probably the more symmetrical 4,4' isomer.

When the volatile diamine mixture was used to cure 2,2-bis(epoxypropoxyphenyl)propane (Epon X-24), the cured resins were quite brittle; however, the undistilled reaction product (which contained higher telomers) or the nonvolatile higher telomers alone produced tough resins.

Further efforts at synthesis were thus directed to the preparation of higher telomers only. This was accomplished by using various molar ratios of amine to formaldehyde between 1 and 2. One-to-one molar ratios were of no interest, because they produce high polymers.

After synthesis and evaluation of these condensation products it was demonstrated that the lower was the molar ratio of *N*-methylaniline to formaldehyde the better did the condensation product function as a curing agent relative to its high-temperature dielectric properties. This was attributed to the gradual increase in the degree of polymerization (D.P.) of the condensation product as the ratio approached the value 1; furthermore, the higher the degree of polymerization, the higher the second-order glass transition temperature of the prepolymer that could be expected, and the higher the second-order glass transition temperature that might be expected of the cured epoxy resin made therefrom. The gradual improve-

ment of dielectric properties as the D.P. of the curing agent increased thus may be due to this factor. It would, of course, be necessary to measure the various second-order glass transition temperatures of cured resins, in order to support this explanation.

There is, of course, another highly plausible explanation of this effect. Since inhibited formaldehyde, which contains methanol, was used in these experiments, it is quite possible that, as the relative formaldehyde concentration was increased, condensation products had successively higher degrees of *N*-methylation. This is illustrated as follows:
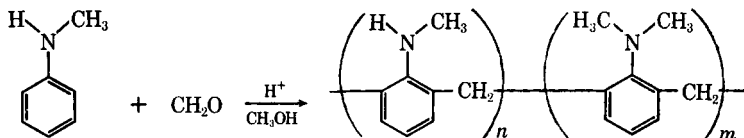
Tertiary amino groups in these prepolymers would, of course, not be capable of adding to epoxy groups, although they would still be catalytic. However, the polyfunctional nature of the products would permit them to continue to function in a curing capacity through additions of the unchanged secondary amino groups.

This explanation could be tested by studying condensation products derived from uninhibited formaldehyde. A comprehensive study of this type was not made, although two such experiments were carried out in which the ratio of *N*-methylaniline to formaldehyde was 1.59 and 1.38.

Dielectric properties of epoxy resins made from these amines again indicated that the lower ratio was superior. Thus it appears that the degree of polymerization is a more important factor in bringing about improved high-temperature dielectric properties than is the extent of methylation. It should also be pointed out that methylation with methanol can also occur on the ring under acid catalysis as well as on the amino groups. If this occurs, the secondary amino groups remain unalkylated and can continue to cure through addition across epoxy groups. It should also be noted that condensations carried out under nitrogen yield very light-colored products, which are capable of producing almost colorless cured epoxies. Distillation of the *N*-methylaniline under nitrogen prior to use also helps considerably in providing chromophore-free polyamines.

After a series of these polyamines were prepared, several experiments were carried out to determine the optimum ratio of the *N*-methylaniline formaldehyde to the epoxy compound. For these tests the curing agent that was used had a molar ratio of amine to formaldehyde of 1.5. When the epoxy/amine equivalent weight ratio exceeded 2, the reaction products were brittle and melted below 100°C.; however, when this ratio was between 1 and 1.5, tough resins were formed.

Optimum dielectric properties were observed when the epoxy/amine equivalent weight ratio was 1. The data are presented in Table I. Data were also obtained from two specimens that were filled with glass micro-

TABLE I
Dielectric Properties of Several Early Epoxies Cured with
N-Methylaniline Formaldehyde

Specimen no.	Epoxy/ amine,[a] eq. wt.	Dielectric constant at 1 kc./sec.		Dissipation factor, %		Insulation resistance,[b] Mohms	
		25°C.	100°C.	25°C.	100°C.	25°C.	100°C.
10	1.00	3.9	3.9	0.5	0.2	$>1 \times 10^7$	3×10^6
3	1.13	4.5	4.8	0.5	0.3	$>1 \times 10^7$	2×10^6
2	1.50	4.5		0.3	4.9	5×10^6	3×10^3
4	2.27			Brittle cracked specimen			
5	5.00			No cure			

[a] Epon X-24 (Shell Chemical Co.).
[b] At 500 volts d.c.

TABLE II
Dielectric Properties of Several Early Epoxies Cured with
N-Methylaniline Formaldehyde (Filled)

Specimen no.	Epoxy/ amine,[a] eq. wt.	Dielectric constant at 1 kc./sec.		Dissipation factor, %		Insulation resistance,[b] Mohms	
		25°C.	100°C.	25°C.	100°C.	25°C.	100°C.
7	1.00	4.0	3.8	0.4	0.1	1×10^7	5×10^6
9 (Distilled diamine)	1.00	3.5	4.9	4.1	34	6×10^5	2×10^3
1	1.50	3.8	4.8	2.5	28	7×10^5	7×10^2

[a] Filled with Eccospheres R.
[b] At 500 volts d.c.

balloons (Eccospheres R, from Emerson and Cuming) and are presented in Table II.

From these data several conclusions may be drawn. The first is that the distilled diamine, bis(methylamino)diphenylmethane, is highly inferior to the polyamine. This is quite apparent in a comparison of the results from specimens 9 and 7. Diamine-cured epoxies were too brittle (unfilled) to yield useful test specimens. A comparison of results from 1 and 7 further demonstrated the superiority of the 1:1 epoxy/amine equivalent weight ratio of reactants over the 1.5:1 ratio.

A more comprehensive study of these curing agents was subsequently undertaken in which in all cases an equivalent weight ratio of Epon X-24 to methylaniline formaldehyde of 1:1 was used. Theoretical equivalent weights were used for the methylaniline formaldehyde condensation products. The dielectric constants, dissipation factors, and insulation resistances of the cured epoxies are graphically illustrated in Figures 1, 2, and 3, respectively. Each of these sets of data verifies the superiority of
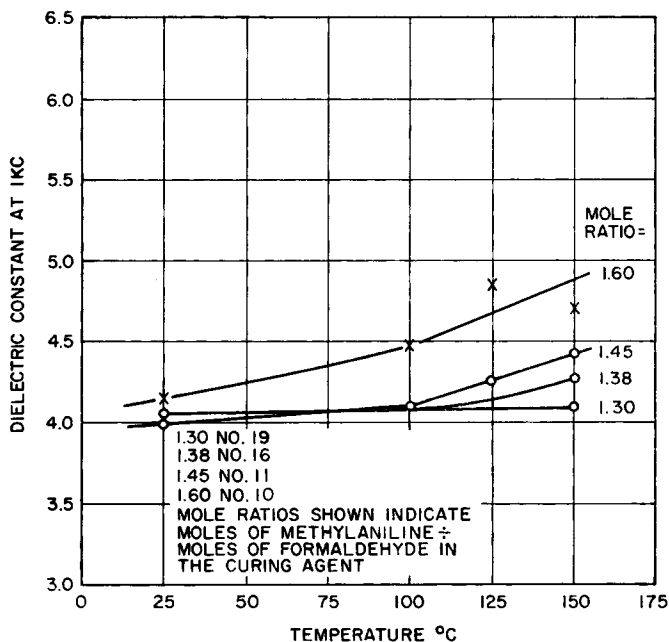
Fig. 1. Dielectric constants of Epon X-24 cured with *N*-methylaniline, as a function of temperature.

the lower methylaniline formaldehyde ratios over the higher ratios. The major improvement was observed at temperatures above 100°C.; below this temperature little advantage of ratio changes was noted. Efforts were also made to study condensation products in which the methylaniline-to-formaldehyde mole ratio was below 1.3. However, these materials were solids with melting points and viscosities in the molten state too high to permit them to be used conveniently. Graphical comparisons of observed dielectric properties are shown in the above-mentioned figures.

The compositions of the various dielectric test specimens are presented in Table III, and a tabulation of additional dielectric test data is presented in Table IV.

One series of dielectric tests was carried out under high vacuum (10^{-6} torr). The data are presented in Table V. The samples used in these tests (No. 10) had been tested previously in air. The aniline formaldehyde curing agent in this case was one having an amine to formaldehyde ratio of 1.6. Differences between the results of these tests and the results obtained in air were of a minor nature.

Several physical property measurements have also been made with Epon X-24 cured with a 1.30 mole ratio of *N*-methylaniline to formaldehyde. The amine was derived from inhibited formaldehyde. The results are compared with those obtained with a 1.60 mole ratio condensation product and are given in Table VI.

TABLE III. Composition of Epoxy Resins Cured with *N*-Methylaniline Formaldehyde

Code	Epoxy/amine, eq. wt.	Amine/CH$_2$O, mole ratio	Resin[a]	Wt., g.	Eq.	Filler	Cure schedule	Comments
1	1.5	1.60	X-24 A	15.4 6.9	0.09 0.06	Ecco. R[b]	74°C., 3 days	Vacuum fill, white, tough
2	1.5	1.60	X-24 A	23.1 10.3	0.136 0.09	—	74°C., 16 hr. + 8 hr. at 100°C.	Light yellow tint, somewhat flexible at 100°C., tough
3	1.1	1.60	X-24 A	23.1 13.8	0.136 0.12	—	74°C., 16 hr. + 8 hr. at 100°C.	Light yellow tint, tough, more than 2 but still flexible at 100°C.
4	2.3	1.60	X-24 A	23.1 6.9	0.136 0.06	—	74°C., 16 hr. + 8 hr. at 100°C.	Fluid at 100°C., very brittle at 25°C., light yellow tint
5	5.0	1.60	X-24 A	30.8 4.6	0.20 0.04	—	75°C., 16 hr. + 8 hr. at 100°C.	No cure, fluid at 25°C.
6	1.0	2.00	X-24 B	17.0 11.3	0.10 0.10	—	74°C., 48 hr.	Very brittle, cracked, light yellow tint
7	1.0	—	X-24 C	17.0 11.3	0.10 0.10	Ecco. R	74°C., 48 hr.	Tough, amber color
8	1.0	2.00	X-24 B	17.0 11.3	0.10 0.10	—	74°C., 16 hr.	Very brittle, cracked
9	1.0	2.00	X-24 B	17.0 11.3	0.10 0.10	Ecco. R	74°C., 16 hr.	Vacuum fill, cracked
10	1.0	1.60	X-24 D	34.0 23.4	0.20 0.20	—	74°C., 16 hr. in N$_2$, 140°C. 3 hr. vacuum	Tough, vacuum fill, amber color
11	1.0	1.45	X-24 F	18.7 13.2	0.11 0.11	—	75°C., 21 hr.; 100°C., 3 hr.	Very tough, very light color
12	1.1	1.38	X-24 G	18.7 11.3	0.11 0.10	—	85°C., 18 hr.; 100°C., 6.5 hr.	Clear, no voids, good specimen
13	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11	—	85°C., 16 hr.; 100°C., 6.5 hr.	No voids, some evidence of unmixed amine

No.	Resin		1.0	0.11		Filler	Cure	Remarks
14	X-24	1.38	1.0	0.11	18.7	Al₂O₃	85°C, 21.5 hr.;	Filler vibrated full and impregnated, no voids, good specimen
	G			0.11	12.6		100°C, 6 hr.	
15	X-24	1.30	1.0	0.11	18.7	Al₂O₃	85°C, 16 hr.,	Filler vibrated in, but only about 95% filled, no voids
	H			0.11	12.6		100°C, 6 hr.	
16	X-24	1.38	1.0	0.11	18.7	—	85°C, 18 hr.;	No voids, good specimen
	G			0.11	12.6		100°C, 6 hr.	
17	X-24	1.38	1.0	0.11	18.7	"OO" smoked silica, 31.3 g.	85°C, 16 hr.;	No voids, some packing of filler at bottom
	G			0.11	12.6		100°C, 6 hr.	
18	X-24	1.38	1.0	0.11	18.7	"OO" smoked silica, 62.6 g.	85°C, 20 hr.;	No voids, some packing of of filler at bottom
	G			0.11	12.6		100°C, 6 hr.	
19	X-24	1.30	1.0	0.11	18.7	—	85°C, 17.5 hr.;	No voids, good specimen
	H			0.11	12.6		100°C, 6 hr.	
20	X-24	1.30	1.0	0.11	18.7	Al₂O₃	85°C, 16 hr.;	Filler vibrated in, no voids, good specimen
	H			0.11	12.6		100°C, 6 hr.	
21	X-24	1.30	1.0	0.11	18.7	"OO" smoked silica, 62.6 g.	85°C, 15.5 hr.;	No voids, good specimen
	H			0.11	12.6		100°C, 6 hr.	
22	X-24	1.38	1.0	0.11	18.7	Ecco. R, 8 g.	85°C, 17 hr.;	One small cavity but was filled
	G			0.11	12.6		100°C, 6 hr.	
23	X-24	1.30	1.0	0.11	18.7	Ecco. R, 8 g.	85°C, 20 hr.;	Several cavities but were filled
	H			0.11	12.6		100°C, 6 hr.	
24	X-24	1.59	1.0	0.11	18.7	—	85°C, 17 hr.;	No voids, good specimen
	I			0.11	12.6		100°C, 6 hr.	
25	X-24	1.38	1.0	0.11	18.7	—	85°C, 16 hr.;	No voids, good specimen
	J			0.11	12.6		100°C, 6 hr.	
26	X-24		1.0	0.11	18.7	—	85°C, 16 hr.;	No voids, good specimen
	K			0.11	12.6		100°C, 6 hr.	
27	X-24	1.59	1.0	0.11	18.7	"OO" smoked silica, 62.6 g.	85°C, 65 hr.;	No voids, some settling of filler
	I			0.11	12.6		100°C, 3 hr.	
28	X-24	1.38	1.0	0.11	18.7	"OO" smoked silica 62.6 g.	85°C, 64 hr.,	No voids, some settling of filler
	J			0.11	12.6		100°C, 3 hr.	
29	X-24	1.38	1.0	0.11	18.7	"OO" smoked silica, 62.6 g.	85°C, 63 hr.,	No voids, some settling of filler
	K			0.11	12.6		100°C, 3 hr.	

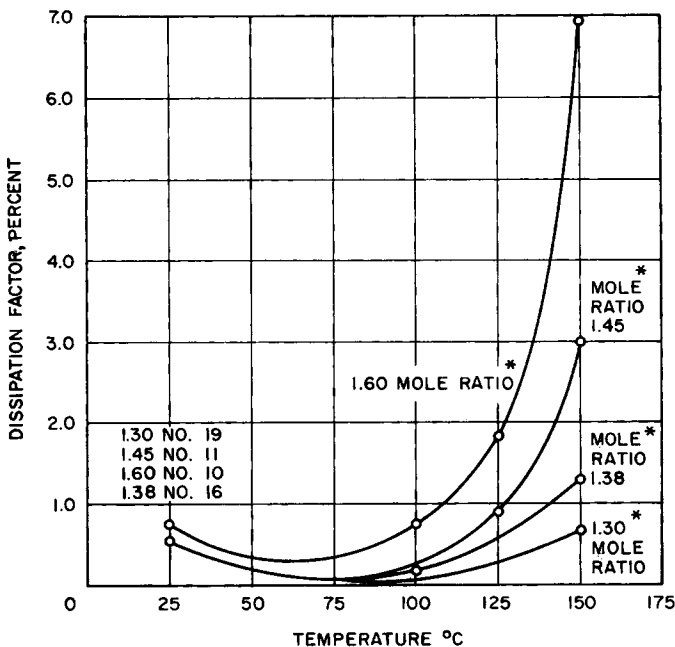Fig. 2. Dissipation factors as a function of temperature. Epon X-24 cured with N-methylaniline formaldehyde. Mole ratios refer to methylaniline/formaldehyde mole ratio. The amines were formulated with the epoxy compound on a 1:1 eq. wt. basis.

Other physical test data on the 1.60 mole ratio product include the following:

1. Elongation, 10%;
2. Compressive yield strength, 5640 psi;
3. Modulus of elasticity, 1.2×10^6 psi;
4. Thermal conductivity, 3.46×10^{-4} cal./sec./cm.^{2}/°C./cm.;
5. Coefficient of expansion, 25–100°C., 0.639×10^{-4} in./in./°C.; $-75-25$°C., 0.502×10^{-4} in./in./°C.;
6. Weight loss at 2×10^{-6} torr (>178 hr. total, >73 hr. at 150°C.) 0.11%.

Also studied was the resistance of two Epon X-24 specimens cured with N-methylaniline formaldehyde to ethylene oxide–Freon mixtures. The tests were conducted according to the new Voyager specifications; the results are shown in Table VII.

Microwave-frequency dielectric tests were also carried out using a specimen of Epon X-24 cured with N-methylaniline formaldehyde (1.30 mole ratio), which had been machined to a flat disk 2.135 in. in diameter by 0.333 in. thick, to allow permittivity measurements in an X-band resonant-cavity dielectrometer. The thickness was chosen on the basis of an estimated dielectric constant of 4.0, to provide a half-wave ($\lambda/2$) specimen. The diameter was chosen to conform to the cavity diameter (2.1609 in).

TABLE IV

Dielectric Properties of Various Epoxy Resins Cured with N-Methylaniline Formaldehyde

Code	Dielectric constant, at 1 kc./sec. (at °C.)				Dissipation factor, % (at °C.)				Insulation resistance,[a] Mohm (at °C.)				Filler,[b] %	Ratio[c]
	25	100	125	150	25	100	125	150	25	100	125	150		
11	4.0	4.1	4.3	4.4	0.5	0.2	0.9	3.0	5×10^7	1×10^7	1×10^5	4×10^3	—	1.45
10	3.9	3.9			0.5	0.2			$>10^7$	3×10^6			—	1.60
16	4.1	4.1	4.1	4.3	0.5	0.1	0.2	1.3	$>10^7$	1×10^7	2×10^5	3×10^4	—	1.38
19	4.1	4.1	4.1	4.2	0.5	0.2	0.2	0.6	$>10^7$	1×10^7	1×10^6	4×10^4	—	1.30
24	4.1	4.2	4.2	4.7	0.8	0.1	0.5	3.5	5×10^7	7×10^6	2×10^5	1×10^3	—	1.59[d]
25	4.2	4.2	4.2	4.5	0.7	0.1	0.3	2.4	5×10^7	5×10^6	18×10^5	1×10^4	—	1.38[d]
14	6.7	6.8	6.8	6.9	0.2	0.1	0.1	0.9	5×10^7	1×10^7	1×10^4	4×10^4	76 A'	1.38
15	6.9	7.0	7.0	7.1	0.2	0.1	0.2	0.7	$>10^7$	5×10^6	0.7×10^6	4×10^4	76 A'	1.30
17	5.4	5.4	5.5	5.5	0.4	0.1	0.4	0.5	$>10^7$	3×10^7	4×10^5	4×10^4	50 B'	1.38
18	6.3	6.4	6.5	6.6	0.3	0.1	0.6	1.5	5×10^7	1×10^7	4×10^5	2×10^4	67 B'	1.38
21	6.1	6.0	6.2	6.4	0.3	0.1	0.2	1.7	$>10^7$	1×10^7	1×10^6	6×10^4	67 B'	1.30
27	6.2	6.3	6.5	6.9	0.3	0.1	1.0	1.0	5×10^7	5×10^6	9×10^4	4×10^3	67 B'	1.51[d]
28	6.2	6.2	6.3	6.4	0.4	0.1	0.1	0.6	5×10^7	1×10^7	1×10^6	2×10^4	67 B'	1.38[d]
22	4.1	4.3	4.4	4.9	1.1	4.9	7.1	15.9	3×10^6	1×10^6	1×10^5	6×10^3	20 C'	1.38
23	4.1	4.3	4.2	4.9	1.0	4.2	9.0	15.2	4×10^6	1×10^6	1×10^5	3×10^3	20 C'	1.30

[a] At 500 volts d.c.
[b] A', alumina; B', "OO" smoked silica; C', Eccospheres R.
[c] Ratio refers to N-methylaniline to formaldehyde; all epoxies were formulated stoichiometrically.
[d] Uninhibited formaldehyde was used in preparing this curing agent.

Volume resistivity was measured with a three-electrode system according to Specification ASTM D 257–61 with polished copper electrodes firmly pressed against the specimen.   The contact area of the guarded electrode
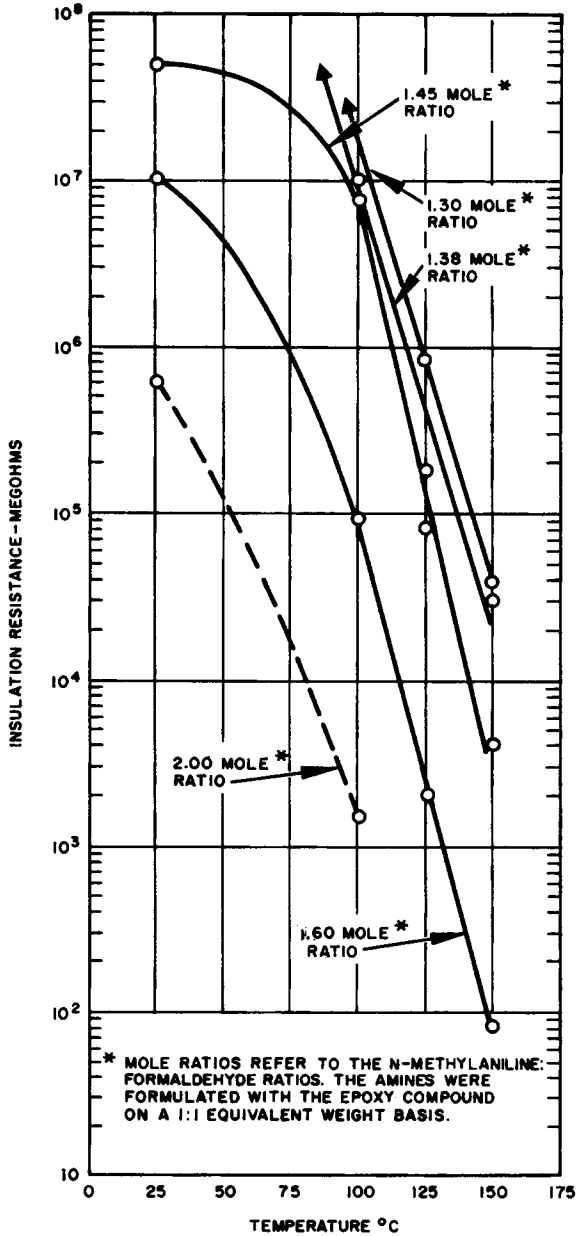

Fig. 3. Insulation resistance as a function of temperature for Epon X-24 cured with *N*-methylaniline formaldehyde.

TABLE V

Dielectric Properties of Epon X-24 Cured with *N*-Methylaniline
Formaldehyde under Vacuum (10^{-6} torr), Sample No. 10

	Time, hr., and temp., °C.					
	20, 25	21, 25	57, 100	83, 125	105, 150	178, 150
Pressure, torr	760	6×10^{-7}	9×10^{-6}	4×10^{-6}	1×10^{-6}	3×10^{-6}
Dielectric constant at 1 kc./sec.	4.1	4.1	4.4	4.9	4.7	4.7
Insulation resistance, Mohm	2×10^4	$>1 \times 10^7$	1×10^5	1×10^3	0.8×10^2	1×10^2
Dissipation factor, %	0.74	0.74	0.76	1.8	8.0	7.4

TABLE VI

Amine/ Epon, eq. wt.	Methylaniline formaldahyde ratio	Compressive strength, psi	Tensile strength, psi	Elastic modulus, psi
1:1	1.30[a]	15,400	14,100	1.1×10^6
1:1	1.60[b]	14,500	12,200	3.7×10^6

[a] Amine H.
[b] Amine A.

TABLE VII

Amine/ Epon, eq. wt.	Methylaniline formaldehyde ratio	Change after six 24 hr. cycles at 40°C.		Change after 168 hr. at 135°C.	
		Wt., %	Vol., %	Wt., %	Vol., %
1:1	1.38	+0.163	−0.03	−0.108	−0.71
1:1	1.30	+0.144	+0.45	−0.104	+0.45

TABLE VIII

Temp., °C.	Dielectric constant	Loss tangent	d.c. Volume resistivity, ohm-cm.
23	3.26	0.053	1.4×10^{15}
67	3.66	0.145	—
23[a]	3.27	0.053	—

[a] After the heat test.

was 10 cm.², and the test voltage was 100 v. d.c.   The current readings
were essentially constant 4 min. after application of voltage.

Permittivity measurements were made at 9.28 Ghz (9.28×10^9 cps)
in an Invar variable-length cavity resonator operating between TE_{014}
and TE_{015} modes.   The cavity is tuned to resonance with and without the

specimen. The shift in resonance length is a function of the specimen dielectric constant. The half-power bandwidth at resonance with the specimen in the cavity is a measure of the dielectric losses in the specimen. Measurements were made at specimen temperatures of 23, 67, and again 23°C. The results of these tests are presented in Table VIII.

The complex permittivity of the dielectric specimen is defined by

$$\epsilon = \epsilon' - j\epsilon'' \tag{3-1}$$

where ϵ' and ϵ'' are the real and imaginary components, respectively. Values relative to vacuum (permittivity $= \epsilon_0$) are defined by

$$\epsilon/\epsilon_0 = \bar{\epsilon} = \bar{\epsilon}' - j\bar{\epsilon}'' = \bar{\epsilon}'(1 - j \tan \delta) \tag{3-2}$$

where $\bar{\epsilon}'$, and $\bar{\epsilon}''$, and $\tan \delta$ denote the relative dielectric constant, relative loss factor, and loss tangent, respectively.

Since the permittivity of air, ϵ_{air}, is almost, but not quite, the same as that of vacuum, dielectric constant values of a specimen relative to air are approximately the same as those relative to vacuum. The permittivity of air varies with several factors, including humidity content and temperature. The values of specimen dielectric constant reported herein are relative to air; that is,

$$\bar{\epsilon}'_{s,air} = \epsilon'_{specim}/\epsilon'_{air}$$

The loss tangent, defined by

$$\tan \delta = \epsilon''/\epsilon' = \bar{\epsilon}''/\bar{\epsilon}' \tag{3-3}$$

is equivalent to the dissipation factor. The latter, for convenience, is often expressed as a percentage.

Calculation of the specimen relative dielectric constant was made by means of the following expression:

$$\bar{\epsilon}_{s,air} = \frac{\epsilon'_s}{\epsilon'_{air}} = (\beta_s^2 + k^2)/(\beta_g^2 + k^2)[1 - \{(\beta_s^2 + k^2)/\beta_s^2\}(\tan^2 \delta 4)/] \tag{3-4}$$

where β_s = phase constant in specimen, β_g = phase constant in cavity (guide), and k = transverse wave number. The value of β_g was calculated from the measured guide wavelength λ_g by

$$\beta_g = 2\pi/\lambda_g = \pi/(\text{TE}_{015} - \text{TE}_{014}) \tag{3-5}$$

The value of k is determined from

$$k = x_1/a \tag{3-6}$$

where a is the cavity radius, and x_1 is equal to 3.8317, the least root of the Bessel function $J_1(x)$.

The value of β_s was calculated from the following transcendental equation:

$$(\tan \beta_s b)/\beta_s b = -[\tan \beta_g(X - b)]/\beta_g b \tag{3-7}$$

where $X = l - L$, l is the TE_{015} resonance length with specimen in the cavity, and L is the length of the empty cavity in the TE_{014} mode.

For low-loss specimens ($\tan \delta \ll 1$) eq. (3-4) simplifies to

$$\bar{\epsilon}'_{s,\text{air}} \approx (\beta_s{}^2 + k^2)/(\beta_g{}^2 + k^2) \tag{3-8}$$

Dielectric constant values obtained with eq. (3-8) were used in eq. (3-9) to calculate the loss tangent. In turn these loss tangent values were used in eq. (3-4) to obtain values of relative dielectric constant (Table VIII).

The loss tangent was calculated from

$$\tan \delta = (\beta_g{}^2/\beta_0{}^2)(1/\bar{\epsilon}'B^2b')(\Delta l - C) \tag{3-9}$$

where β_0 is the free-space phase constant, b' is a modified specimen thickness, related to the actual thickness b by

$$b' = b[1 - (\sin 2\beta_s b)/2\beta_s b] \tag{3-10}$$

B is given by

$$B = [1 + (\beta_s{}^2/\beta_g{}^2 - 1)\cos^2 \beta_s b] \tag{3-11}$$

and C is a (measurable) correction term, generally small with respect to Δl, the half-power bandwidth of the resonance peak.

EXPERIMENTAL

N-Methylaniline Formaldehyde Preparations

A. *N*-Methylaniline (172 g., 1.61 moles) was dissolved in concentrated hydrochloric acid (72 ml., 0.84 mole) and was cooled to 0–5°C. Aqueous formaldehyde solution (37%, 80 g., 1.00 mole, stabilized with 10–15% methanol) was then added dropwise to the amine solution over a $1/2$ hr. period while the temperature was kept at 0–5°C. After completion of the addition the same temperature was maintained for 1 hr. The reaction mixture was then heated at reflux for 8.5 hr., and after cooling it was diluted three times. Sufficient hydrochloric acid was added to yield a clear solution. Then dilute alkali ($\approx 15\%$ NaOH) was added dropwise during vigorous stirring, until the final pH was 8. The precipitated solid was diluted with ethanol (100 ml.) and benzene (500 ml.) and the organic phase that separated was washed with alkali (20% NaOH). After three water washes the solution was dried over Na_2CO_3 and filtered. Solvents were then removed by vacuum distillation (up to 135°C. at 2 torr), yielding a dark amber polyamine weighing 167 g. (91%).

A second batch (A) was prepared under nitrogen in a modified procedure with purer reagents. The details of this rerun are presented below.

N-Methylaniline (186 g., 1.74 moles), which was freshly distilled under nitrogen, was dissolved in concentrated hydrochloric acid (80 ml., 0.93 mole), while a nitrogen atmosphere was maintained. The solution was cooled to 0°C., and uninhibited formalin (37% CH_2O, 88 g., 1.09 moles)

was slowly added while the temperature was kept at 0–5°C. Upon completion of the addition the temperature was maintained for 1 hr.; then the mixture was heated to reflux for 10–11 hr. The solution was then diluted three times with water, and benzene ($\approx$ 350 ml.) was added. It was then neutralized to a phenolphthalein endpoint with 10% NaOH solution. The benzene layer was collected, thoroughly washed with water, and dried with Na$_2$CO$_3$. Benzene was then removed under nitrogen at ambient pressure followed by vacuum (4 torr) at 135°C. The very light tan-colored product weighed 192 g. (95% of theoretical).

B and C. *N*-Methylaniline (172 g., 1.61 moles) was dissolved in concentrated hydrochloric acid (72 ml., 0.84 mole), and the mixture was cooled to 3 ± 2°C. Aqueous formaldehyde (64 g., 37%) was then added slowly at temperatures kept between 0 and 5°C. After the addition was completed, the temperature was maintained below 5°C. for 1 hr. The reaction mixture was then heated to boiling and refluxed for 10 hr. under a nitrogen atmosphere. It was then diluted to 1500 ml. with water, and its pH was adjusted to 7 by the gradual addition of aqueous NaOH solution (20%). The precipitated amine was then extracted with benzene, and the benzene solution was washed with dilute alkali (10% NaOH), followed by distilled water. After drying with potassium carbonate the benzene was removed by simple distillation, and the amine was recovered on a molecular still. An attempted simple distillation of the amine at 1–2 torr and 170°C. proved unsatisfactory (only 6.2 g. of unreacted *N*-methylaniline was recovered). Distillation at 10^{-3} torr and 100–130°C., followed by a subsequent distillation at 150–160°C. at 10^{-3} torr, yielded 153 g. (85%) of a light yellow mixture of bis(methylamino)-diphenylmethane isomers. This portion was designated B. The nonvolatile fraction (25 g.) was designated C.

F. Concentrated hydrochloric acid was gradually added to ice-cold, freshly distilled *N*-methylaniline (334 g., 3.12 moles). The solution was then cooled to 0°C., and the temperature was maintained between 0 and 5°C. while uninhibited formaldehyde (174 g., 2.14 moles, 37%) was gradually added. After the addition was completed, the solution temperature was maintained at 0–5°C. for 1 hr. It was then heated at reflux for 8 hr. and then cooled. After 2 days benzene (500 ml.) was added, and the solution was treated with excess aqueous sodium hydroxide. The benzene phase was separated, washed twice with water, dried azeotropically, cooled, and filtered. Solvent was then removed under vacuum ($\approx$5 torr) during gradual heating to 180°C. The viscous cooled product weighed 320 g. (90% yield).

G. and H. G is the 1.38-mole-ratio prepolymer. Formalin (230 g., 37%, 2.84 moles, inhibited) was added to a solution of redistilled *N*-methylaniline (419 g., 3.92 moles) in aqueous hydrochloric acid (163 ml., 12*M*, 0.96 mole) with the temperature kept at 0–5°C. After 1–1.5 hr. at this temperature the mixture was heated at reflux for 8 hr. Toluene (700 ml.)

was then added and the pH adjusted to 8–10 with sodium hydroxide solution (47 g. per 200 ml. of H_2O). After cooling the toluene phase was separated, washed twice with water, dried azeotropically, filtered, and concentrated under vacuum (8 torr) while the temperature gradually rose to 180°C. The product weighed 390 g. and melted at 40–45°C. It represented an 85% yield.

H. H represents a 1.30-mole-ratio product. The same procedure was used in this preparation, except that 217.5 g. of *N*-methylaniline (2.03 moles), 126.8 g. of formalin (1.564 moles), and 85 ml. of concentrated aqueous hydrochloric acid (1.02 moles) were used. The product weighed 212 g., melted at 53–69°C., and was 88% of theoretical.

I. I represents a 1.59-mole-ratio product derived from uninhibited formaldehyde. The formaldehyde used in this preparation was obtained from the hydrolysis of 200 g. of paraformaldehyde in 500 ml. of water and 10 ml. of concentrated hydrochloric acid. Aliquots of the hydrolyzed paraformaldehyde were used in the next two preparations. This reaction was carried out in the same manner as the first two, except for the reactant quantities, namely *N*-methylaniline (172 g., 1.61 moles), formalin (28.2% 108 g., 1.015 moles), and 12M HCl (61 ml., 0.73 mole). A yield of 166 g. (89%) of a light amber product was obtained.

J. J represents a 1.38-mole-ratio product derived from uninhibited formaldehyde. The reactants used were *N*-methylaniline (204 g., 1.91 moles), formalin (28.2%, 147 g., 1.38 moles), and 12M HCl (79 ml., 0.95 mole). A yield of 206 g. (84%) was obtained.

K. The same as J.

L. Freshly distilled *N*-methylaniline (266 g., 2.49 moles) was dissolved in concentrated hydrochloric acid, and the mixture was cooled to −5°C. Formalin (152 g., 1.87 moles, 37%, uninhibited) was then added at a constant temperature of 5 ± 5°C. After the addition was completed, the reaction mixture was maintained at 5 ± 5°C. for 1 hr. more. It was then heated to boiling and maintained at reflux for 8 hr. Water (100 ml.) was added to the mixture during the course of the reaction, in an attempt at redissolving a large mass of congealed material, but this was not very successful. When the mixture was cooled and the fluid phase decanted, the large mass of polymer was successfully dissolved in concentrated hydrochloric acid (approximately 150 ml.). Both dissolved polymer phases were then recombined, and after twofold dilution with water they were treated with 20–25% sodium hydroxide solution. Precipitated polymer was then dissolved in a mixture of ethanol and benzene, and the solution was washed once with a 10% sodium hydroxide solution and then twice with water. After drying azeotropically the solvents were removed under vacuum while the pot temperature was allowed to approach 175°C. gradually. Because of its hazy appearance, however, the polymer was redissolved in methylene chloride, filtered, reconcentrated under vacuum (to 175°C.), and finally cooled to a resinous mass.

Résumé

Une série d'amines aromatiques secondaires ont été préparées par la condensation, catalysée par les acides, de la N-méthylaniline avec le formaldéhyde. Ces produits de condensation ont été essayés comme agents de traitement pour un prépolymère époxy étalon, à savoir le bis(2,3-époxypropoxyphényl)propane. Différents rapports molaires de N-méthylaniline et de formaldéhyde ont été utilisés pour obtenir des produits de condensation polyaminés, avec des degrés variables de polymérisation. Ces rapports molaires variaient de 1.60 à 1.30. Les propriétés diélectriques des résines époxy post-traitées, à des températures supérieures à 100°C, sont fortement fonction de ces rapports. Des produits de condensation dans un rapport inférieur, produisaient des résines ayant des propriétés diélectriques optimales à température élevée ainsi que de bonnes propriétés physiques.

Zusammenfassung

Eine Reihe von sekundären aromatischen Aminen wurde durch säurekatalysierte Kondensation von N-Methylanilin mit Formaldehyd hergestellt. Es wurde festgestellt, dass diese Kondensationsprodukte als Härtungsmittel für die Vorstufe eines Standard-Epoxypolymeren, nämlich Bis(2,3-epoxypropoxyphenyl)propan, fungieren. Verschiedene Molverhältnisse von N-Methylanilin zu Formaldehyd wurden verwendet, um Polyamin-Kondensationsprodukte mit verschiedenen Polymerisationsgraden darzustellen. Diese Molverhälnisse lagen im Bereich von 1,60 bis 1,30. Bei Temperaturen über 100°C waren die dielektrischen Eigenschaften der gehärteten Epoxyharze stark von diesem Verhältnis abhängig. Kondensationsprodukte mit einem kleineren Molverhältnis ergaben Harze, die bei der höheren Temperatur sowohl optimale dielektrische Eigenschaften als auch gute physikalische Eigenschaften aufwiesen.