

Characterization of Solutions and Aqueous Dispersions of Epoxy/Amidoamine Resins

S. B. A. QADERI, M. C. PAPUTA PECK, and D. R. BAUER,
*Research Staff, Ford Motor Company, P.O. Box 2053,
Dearborn, Michigan 48121*

Synopsis

Molecular weight advancement and epoxy conversion in epoxy-amidoamine resins have been characterized in solutions and in aqueous dispersions using viscosity, light scattering, and near-infrared spectroscopy. By measuring the intensity of the 4532 cm^{-1} band in the near infrared, it is possible to determine the concentration of epoxy groups in these resins at low levels in the presence of amine and acid groups as well as solvents and other species. The epoxy-amine reaction in these resins is found to be second order with an activation energy of around 13 kcal/mole. The addition of one mole of carboxylic acid per mole of amine functionality was sufficient to quench the epoxy-amine reaction. Preparation of aqueous dispersions suitable for electrocoat formulation required that the extent of epoxy reaction be within a given range. Although the addition of acid completely quenched the epoxy-amine reaction, a slow side reaction was discovered which consumes epoxy groups and ultimately changes the physical properties of coatings made from these dispersions.

INTRODUCTION

Mixtures of epoxy and amidoamine resins are widely used in coatings and adhesives. In particular, electrocoat formulations based on bisphenol A-epi-chlorohydrin resins reacted with amidoamines have been prepared in this laboratory.¹ A key aspect of electrocoat formulation with these materials is the addition of acid to the mixture after partial reaction of the epoxy groups with the amine groups on the amidoamine. This prevents further epoxy-amine reaction and allows dispersion of the resin mixture into water.¹ The extent of epoxy conversion (among other variables) mainly determines whether or not a nonsettling dispersion can be formed. After the dispersion is formed, it is necessary to ensure that the epoxy-amine reaction remains quenched to prevent gelation in the dispersion particles. During deposition and subsequent cure, the neutralizing acid is removed from the coating and the epoxy-amine reaction proceeds. Since this is the major crosslinking reaction, the residual epoxy content in the dispersed bath must be maintained.

In this paper, the results of characterization studies of epoxy-amidoamine resins both in solution and in dispersion are described. A variety of techniques are employed including viscosity measurements for determining the molecular weight of the epoxy-amidoamine in solution, light scattering measurements for determining molecular weight in dispersion, and near-infrared spectroscopic measurements of epoxy content in solution and dispersion. Near-infrared spectroscopy has been shown to be a practical way to determine low

levels of epoxy in fully formulated electrocoat baths where the presence of amines and acids make titration impossible and where the epoxy signal at 915 cm^{-1} in the mid-infrared region is obscured by other strong bands.² In this paper, epoxy concentration and viscosity increase are monitored as a function of synthesis time and temperature. The range of reaction conditions which yield acceptable electrocoat dispersions is determined. The level of neutralizing acid necessary to prevent advancement of the epoxy-amine reaction in dispersion is reported. A slow side reaction which consumes epoxy groups without affecting the resin molecular weight is identified.

EXPERIMENTAL

Materials

All resins, reagents, and solvents were used without further purification. The epoxy resins, Epon 1001F, Epon 1002F, Epon 1004F, Epon 1007F, and Epon 1009F were obtained from Shell Chemical Co. Lactic acid was obtained from Fisher Scientific Co. Methylisobutyl ketone was obtained from Aldrich Chemical Co. Hexyl Cellosolve was procured from Union Carbide Corporation. Dipropylene glycol methyl ether was obtained from Dow Chemical Co. Catalyst, EH-330 (tris dimethyl aminomethyl phenol) was obtained from Thiokol Chemical Company. Two different types of amidoamines were used. Amidoamine AA-1 was obtained from Henkel Corp. and amidoamine AA-2 was obtained from Ciba Geigy. The composition of the amidoamines was determined by nitrous acid treatment,³ infrared spectroscopy, and ^{13}C and ^1H nuclear magnetic resonance (NMR). Amidoamine AA-1 has been found to be a reaction product of a long straight chain fatty monocarboxylic acid with a polyamine. Although the exact structure could not be determined, the nitrous acid treatment indicated a high concentration of primary amine groups while the spectroscopic data indicated little unsaturation or formation of imidazoline rings. Amidoamine AA-2 has been found to be a reaction product of a long branched chain fatty monocarboxylic acid and contains high levels of secondary amine groups, unsaturation, aromatic groups, and imidazoline groups.

Epoxy-amidoamine resins can be prepared by dissolving an epoxy resin or blend of resins in a mixture of solvents. The amidoamine is added such that the ratio of epoxy to amine hydrogens is 1 : 1. Total resin solids ranged from 50 to 60 wt%. After reaction for a given time and temperature, lactic acid is added to the reaction mixture to quench the reaction. Deionized water is then added to the neutralized resin mixture and a dispersion is formed. The dispersion can be blended with pigmented resins to form an electrocoat paint.

Characterization Techniques

Viscometry

The apparent viscosity was measured using a Contraves Rheomat 108 rotational viscometer. The unit consists of a bob attached to a measuring head and surrounded by a tube. The bob and the tube were immersed in resin solution. The bob was rotated at a set speed. The built-in microprocessor

calculates shear rate and viscosity as well as other rheological parameters corresponding to the set rotational speed and diameter of bob used. All data were measured at room temperature and 50 wt% solids in a constant solvent mixture.

Light Scattering Apparatus and Methods

The light scattering apparatus consisted of a helium-neon laser (Spectra Physics model 124b), a cell holder, a photomultiplier tube, and a picoammeter. A 1.0 wt% polymer solution was prepared by adding an appropriate amount of the unpigmented dispersion to spectroscopic grade *p*-dioxane. The dioxane dissolved the dispersion and permitted a qualitative measurement of the polymer molecular weight. The scattered intensity was measured at 90° and compared to a standard polystyrene solution. Because of the small radius of gyration of these polymers it was not necessary to determine the intensity as a function of angle. Because of the low molecular weight and thus low scattering intensity it was not possible to accurately measure intensities at a concentration of less than 1%. Since only the relative increase in molecular weight was of interest, the measurement of refractive index increment, dn/dc was not considered necessary. Small, inadvertent variations in cosolvent concentration (which incidentally, can have a significant effect on the dn/dc) limited reproducibility of the light scattering measurement of the weight-average molecular weight to $\pm 20\%$. It was not possible to measure molecular weights in pigmented baths due to strong scattering from residual pigment particles.

Near-Infrared Spectral Determination of Epoxy Concentration

Fourier-transform infrared (FTIR) spectra of the epoxy resin in a solution of chloroform were obtained using a Nicolet 7001 Michelson interferometer interfaced to a DEC PDP-11/60 computer.² Although the epoxy-containing resin solutions were readily soluble in chloroform, the aqueous dispersions were not soluble due to presence of water. Two techniques were employed to remove the water. In one case acetone was added to dispersion and the water-acetone mixture was allowed to evaporate overnight. The residue was then dissolved in chloroform. Reproducibility of this technique was poor for the pigmented dispersions, possibly because of the inability to remove water adsorbed on the pigment particles. A second more successful technique consisted of electrodepositing the dispersion on a clean, bare steel surface.⁴ The electrodeposited film, which is essentially free of water due to electro-osmosis, could then be dissolved in chloroform. Pigment particles were removed from the chloroform solution by ultracentrifugation. Small traces of carbon black particles remained after this treatment. The presence of these particles and the other residual cosolvents did not interfere with the near-infrared epoxy band at 4532 cm^{-1} . A 1.0 wt% solution of the resin was transferred to a glass-stoppered infrared-type quartz cylindrical cell with a 20-mm path length and 22-mm outer diameter for measurement of spectra. The epoxy concentration was determined by measuring the intensity of the epoxy band at 4532 cm^{-1} . Details of the quantification procedure have been described elsewhere.²

RESULTS AND DISCUSSION

Resin Synthesis and Dispersion Preparation

When epoxy resins are mixed with amidoamines, epoxy-amine condensation occurs leading to an increase in molecular weight and viscosity.⁵⁻⁸ If the reaction is allowed to continue, the epoxy-amidoamine resins used in this study will form a gel. In order to form a dispersion it is necessary to quench the epoxy-amine reaction. In practice, this is achieved through the addition of one equivalent of a carboxylic acid such as lactic acid.¹ This neutralizes the amine groups preventing the epoxy-amine reaction. The point at which the acid is added is crucial to dispersion preparation. Dispersions can only be prepared from these materials if the epoxy-amine extent of reaction falls within a certain range. In order to reliably prepare dispersions it is necessary to be able to monitor the extent of epoxy conversion and/or increase in molecular weight as a function of formulation variables and reaction conditions.

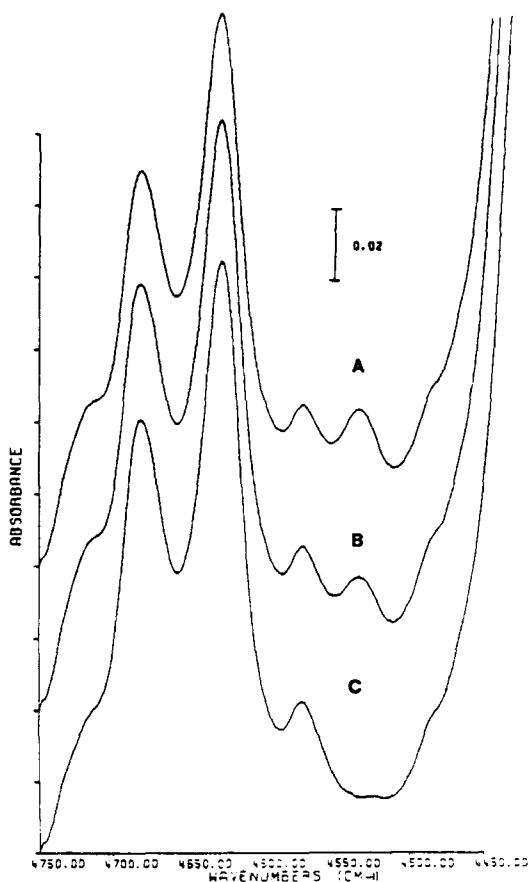


Fig. 1. Near-infrared spectra of epoxy resins. A is the unreacted epoxy resin, B is the resin after 30% reaction with AA-1, and C is an epoxy resin after complete reaction with diethylamine.

TABLE I
Epoxy Conversion Versus Epoxy and Amine Level

Amidoamine	Epoxy level (M ^a)	Amine level (M)	% Epoxy reacted ^b
AA-1	0.27	0.27	18
AA-1	0.38	0.38	25
AA-1	0.42	0.42	30
AA-1	0.45	0.45	28
AA-1	0.42	0.32	18
AA-1	0.42	0.21	10
AA-2	0.42	0.42	15

^a Moles/liter.

^b Conversion after 20 h at 20°C.

The percent epoxy reacted can be followed by measuring the intensity of the near-infrared epoxy absorption band at 4532 cm^{-1} as shown in Figure 1. Measurements of epoxy conversion after reacting for 20 h at 20°C are reported in Table I as a function of epoxy and amine concentration. The epoxy concentration was controlled by varying the molecular weight of the epoxy resin while the amine concentration was controlled by varying the amidoamine resin concentration. The rate of the epoxy-amine reaction is roughly the product of the fraction of epoxy conversion and the initial epoxy concentration divided by the reaction time. The epoxy-amine reaction rate decreases with decreasing epoxy and amine concentration. The reaction rate data are qualitatively consistent with the epoxy-amine reaction being first order in both epoxy and amine concentration in agreement with proposed reaction mechanisms.⁸ The second-order rate constant for AA-1 at 20°C is roughly $10^{-5}\text{ M}^{-1}\text{ s}^{-1}$. The reactivity of AA-2 is roughly half that of AA-1. This is likely due to the fact that AA-1 contains more reactive primary amines while AA-2 contains less reactive secondary amines.

Table II presents epoxy conversion and viscosity data for the two amidoamines reacted with an epoxy resin whose number-average molecular weight is 2420 as a function of reaction time and temperature. The slight variation in epoxy concentration is due to differences in solvent content. Viscosity measurements were taken at 20°C at a constant solids level of 50 wt%. Data on the dispersibility of the resins are also included. Increasing the temperature from 20° to 40°C decreases the reaction time necessary to achieve a given epoxy conversion (e.g., 30%) by a factor of about four. Assuming an Arrhenius expression, this is equivalent to an activation energy for the epoxy-amine reaction of roughly 13 kcal/mole which is typical for epoxy-amine reactions.⁸ As expected, the viscosity increases with increasing epoxy conversion. Surprisingly, the relationship between viscosity (measured at room temperature) and extent of conversion appears to depend on the temperature that the reaction is carried out. At a given extent of reaction, for example at 30%, the viscosity increase is higher in the room temperature preparation than it is in the high temperature preparation. The reason for this difference is not clear. It should be noted that the high temperature reaction mixtures are stirred during reaction while the room temperature reaction is unstirred. The difference does not appear to affect dispersibility or final electrocoat properties.

TABLE II
Epoxy Conversion and Viscosity Increase Versus Reaction Time and Temperature

Amidoamine	Epoxy level M	Temp. (°C)	Time (h)	Viscosity ratio ^a	% Epoxy reacted	Dispersibility	Predicted M_w ratio ^b
AA-1	0.42	20	20	2.2	30	yes	—
AA-1	0.42	40	2	1.33	—	—	—
AA-1	0.42	40	5	2.08	—	—	—
AA-1	0.42	40	7	4.02	—	—	—
AA-1	0.39	40	5	1.84	—	—	—
AA-1	0.36	40	3	1.26	17	no	1.23
AA-1	0.36	40	4	1.51	24	yes	1.42
AA-1	0.36	40	5	1.65	30	yes	1.66
AA-1	0.36	40	6	1.88	39	yes	2.21
AA-1	0.36	40	7	1.97	—	no	—
AA-2	0.42	20	20	1.90	15	yes	—
AA-2	0.39	50	2	1.57	12	yes	1.42
AA-2	0.39	50	3	1.63	17	yes	1.70
AA-2	0.39	50	4	1.71	22	no	2.2
AA-2	0.39	50	5	2.0	23	no	2.4
AA-2	0.39	50	6	2.8	24	no	2.6

^a $\text{vis}(t = t) / \text{vis}(t = 0)$

^b $M_w(t = t) / M_w(t = 0)$, the predicted molecular weight increases are calculated from Ref. 9 assuming a functionality of 3 for AA-1 and 7 for AA-2.

The relationship between viscosity increase and extent of conversion also depends on the nature of the amidoamine. At any degree of conversion, the viscosity increase is greater for AA-2 than AA-1. In theory⁹ the molecular weight advancement of a crosslinking mixture depends on the extent of reaction and the number of functional groups per molecule. With expressions in the literature,⁹ it is possible to calculate molecular weight increases for the epoxy-amidoamine resins as a function of the extent of epoxy conversion and amidoamine functionality (the epoxy functionality being 2). Molecular weight increases compare well with viscosity increases if the functionalities of AA-1 and AA-2 are roughly 3 and 7, respectively. Considering that the increase in viscosity may not necessarily be proportional to the increase in molecular weight, these derived functionalities have to be considered at best approximate.

As noted in Table II, the resin mixtures form a nonsettling aqueous dispersion over a limited range of epoxy conversion. For AA-1 the range is roughly 24–39% while for AA-2 it is roughly 12–17%. Dispersibility at high extent of conversion appears to be limited by the molecular weight of the resin. At the maximum extent of conversion for dispersibility the viscosity increase is roughly the same for the two amidoamines. It is known that higher molecular weight resins are harder to disperse in water than low molecular weight resins.¹⁰ The maximum extent of conversion for AA-2 is less than that for AA-1 because the viscosity (and thus molecular weight) increases faster with extent of reaction.

Dispersibility at low conversion may be limited by the requirement that a certain fraction of the amidoamine must be bound to the epoxy. The amidoamine-lactic acid salt in essence acts as a surfactant to disperse the

epoxy resin. Since there is a minimum level of epoxy-amine reaction required to achieve a dispersion, the amidoamine-lactic acid salt must be a better surfactant for the epoxy resin after it has reacted with the epoxy resin. With the use of the epoxy conversion and the amidoamine functionality derived above, it is possible to estimate the fraction of amidoamine molecules that have not reacted with an epoxy group. At their respective minimum extents of conversion, this fraction is roughly 40% for both AA-1 and AA-2. This means that roughly 60% of the amidoamine molecules must be bound to an epoxy resin molecule in order to achieve an acceptable dispersion in this system.

Dispersion Stability

In the above studies, dispersions have been prepared using 100% neutralization. In typical electrocoats, the acid is simply present to promote dispersion and the extent of neutralization is less than 100%, usually around 75%.⁴ In the epoxy-amidoamine electrocoat, the acid is also necessary to prevent the epoxy-amine reaction. It has been found that a substantial improvement in corrosion protection and "throwpower" performance could be achieved in the

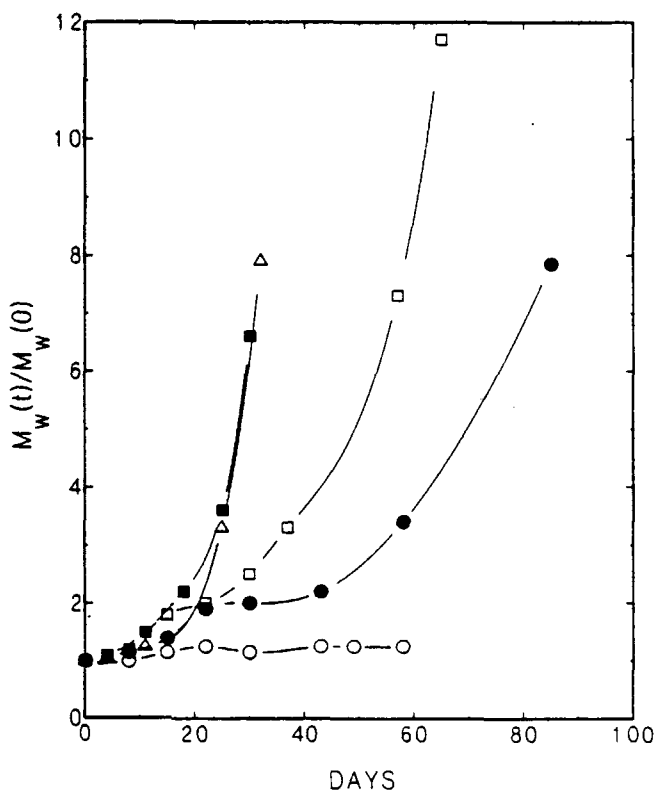


Fig. 2. Increase in weight-average molecular weight versus time. The neutralizing acid is lactic acid and the catalyst is EH-330. The neutralization and catalyst levels are 100% and 0.0% (\circ), 87.5% and 0.0% (\square), 75% and 0.0% (\triangle), 100% and 0.2% (\bullet), and 87.5% and 0.2% (\blacksquare). The acid level is based on amine functionality while the catalyst level is a weight percent based on resin solids.

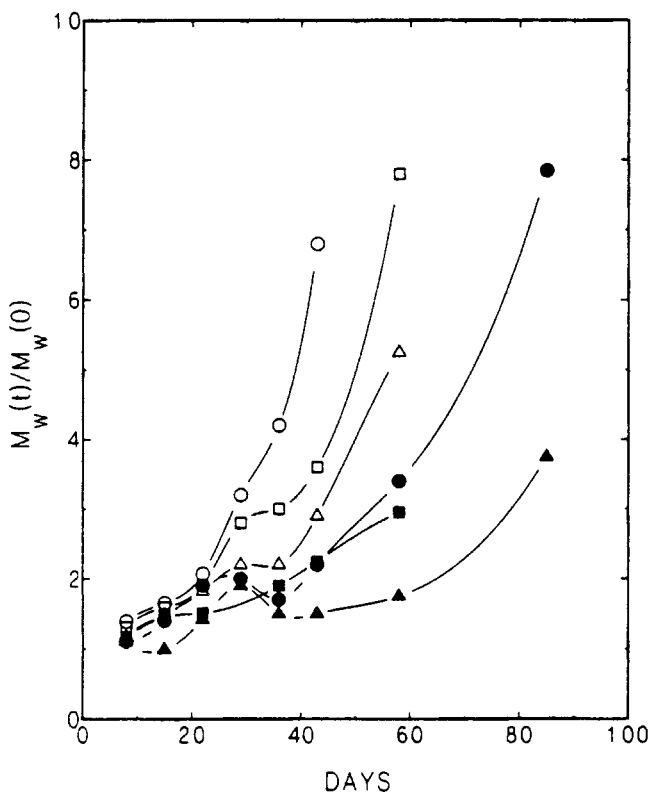


Fig. 3. Increase in weight-average molecular weight versus time. The neutralization and catalyst level are 100% and 0.2%, respectively. Of the neutralizing acid, 75% is lactic acid while the other 25% is pivalic (○), octanoic (□), acetic (△), lactic (●), formic (■), and trichloroacetic (▲).

epoxy-amidoamine electrocoat if the level of neutralization could be lowered to 75%. In addition it has been found that the bake temperature could be reduced through the use of catalysts such as EH-330. To determine the effect of lower acid levels and presence of catalyst on the rate of the epoxy-amine reaction in the dispersion, the weight-average molecular weight of the epoxy-amidoamine resin was followed as a function of time using light scattering. The results are shown in Figures 2 and 3. As shown in Figure 2, the molecular weight of the resin in underneutralized dispersions increases with time. As the molecular weight increases, the electrodeposited film becomes very rough and thin. The rate of molecular weight increase depends on the extent of underneutralization and also increases with the presence of catalyst. In the presence of catalyst, even 100% neutralization is insufficient to maintain molecular weight stability. As shown in Figure 3, the use of stronger acids to neutralize a fraction (25%) of the amines does improve the stability in the presence of the catalyst, however, molecular weights increase eventually even when very strong acids ($pK = 0.7$) are used. Achievement of a molecular weight stable dispersion in the epoxy-amidoamine electrocoat requires 100% neutralization and precludes the use of a catalyst.

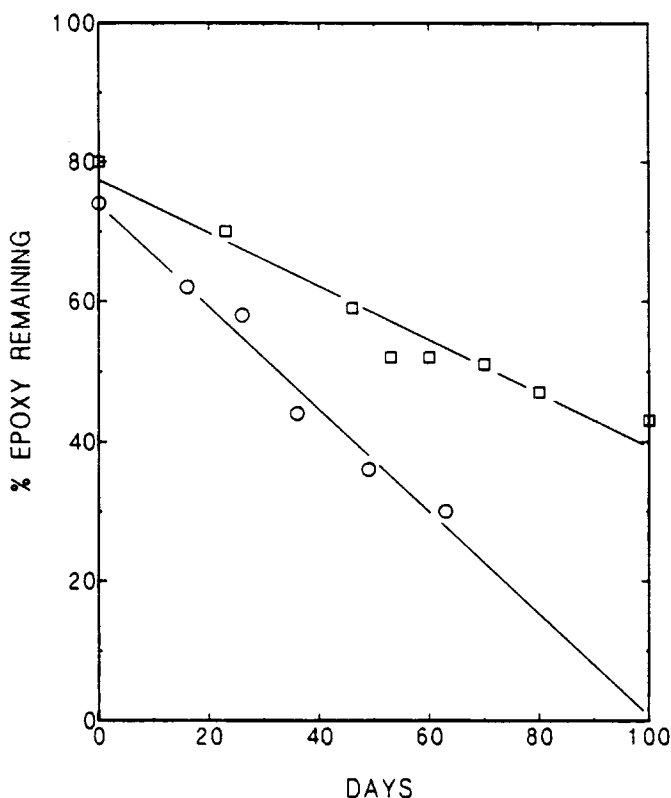


Fig. 4. Percent of epoxy groups remaining in the electrocoat dispersion versus time for AA-1 (○) and AA-2 (□). The electrocoat baths are 100% neutralized and contain no catalyst.

Even molecular weight-stable baths have been found to exhibit slow changes in electrodeposition and other physical properties. The electrodeposition voltage required to achieve a given film thickness (as measured using a Fischer-type Es 8e 3G Permascope) slowly increased and the solvent resistance of the cured films slowly decreased with time. The loss of solvent resistance suggested a decrease in crosslink density. As shown in Figure 4, the loss of solvent resistance is due to the slow consumption of epoxy groups in the 100% neutralized bath. The rate of disappearance of epoxy functionality is a function of amidoamine type. The rate is roughly three-times slower for AA-2 than for AA-1. The difference in the rate of consumption of epoxy correlates with the rate of change of electrodeposition behavior. As shown in Figure 5, the rate of decrease in film thickness as a function of aging time (at constant deposition conditions¹⁰) is three-times faster in the bath prepared with AA-1 than with AA-2.

The exact reaction responsible for the slow consumption of epoxy groups is not known. Since the molecular weight is not increasing, the reaction cannot be between epoxy and amine groups. It is possible that the reaction is between epoxy groups and hydroxy groups from the solvents or water and that this reaction is catalyzed by the acid-amidoamine salt. Although the rate of

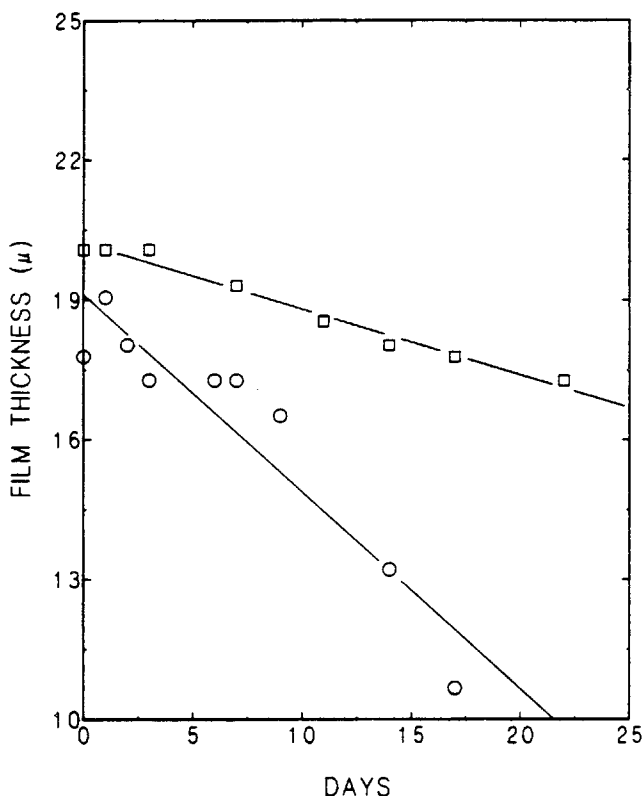


Fig. 5. Deposited film thickness versus time for electrocoat baths containing AA-1 (○) and AA-2 (□). Films were deposited at 200 volts for 2 minutes.

reaction is relatively slow, over the course of a few months enough epoxy is consumed to significantly change coating properties.

CONCLUSION

The synthesis and aqueous dispersions of epoxy amidoamine resins have been characterized by near-infrared spectroscopy, viscosimetry, and light scattering. The extent of epoxy conversion and the molecular weight increase during epoxy-amidoamine reaction have been followed as a function of time and temperature. The reaction is found to follow second-order kinetics with an activation energy of 13 kcal/mole. The relation between the extent of epoxy conversion and the increase in viscosity is used to estimate the functionality of the amidoamine resins. The epoxy-amidoamine reaction is quenched by the addition of acid. A 100% neutralization was required to prevent further epoxy-amidoamine reaction in solution and after dispersion preparation. Acceptable dispersions could be prepared only over a limited range of epoxy conversion. Although the epoxy-amidoamine reaction could be quenched by 100% neutralization with acid, it is found that the concentration of epoxy groups in the bath slowly decreased with time. It is suggested that this is caused by a slow solvolysis or hydrolysis of the epoxy group. The slow

disappearance of epoxy functionality accounts for the decrease in solvent resistance of cured coatings with time.

References

1. R. A. Swider and M. E. Horsch, U.S. Patent 4,568,710, Feb. 4, 1986.
2. M. C. Paputa-Peck, R. O. Carter III, and S. B. A. Qaderi, *J. Appl. Polym. Sci.*, **33**, 77 (1987).
3. J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin Inc., New York, 1965, p. 665.
4. P. Pierce, *J. Coat. Technol.*, **53** (672), 52 (1981).
5. Y. Tanaka and T. F. Milka, in *Epoxy Resins, Chemistry and Technology*, C. A. May and Y. Tanaka, Eds., Marcel Dekker Inc., New York, 1973.
6. J. W. Holubka and R. A. Dickie, *J. Coat. Technol.*, **56** (716), 87 (1984).
7. H. Lee and K. Neville, *Handbook of Epoxy Resins 10-3*, McGraw Hill Book Co., New York 1967.
8. J. M. Barton, in *Advances in Polymer Science* Vol. 72, K. Dusek, Ed., Springer-Verlag, Berlin, 1985, p. 111.
9. C. W. Macosko and D. R. Miller, *Macromolecules*, **9**, 199 (1976).
10. S. B. A. Qaderi, D. R. Bauer, J. W. Holubka, and R. A. Dickie, *J. Coat. Technol.*, **56** (719), 71 (1984).

Received October 17, 1986

Accepted December 11, 1986