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ROBERT F. HERRICK & THOMAS J. SMITH

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Development of a Sampling and Analytical Method for Measuring the Epoxy Content of Aerosols: I. Development of the Analytical Method*

ROBERT F. HERRICK[A] and THOMAS J. SMITH[B]

[A]National Institute for Occupational Safety and Health, Division of Surveillance, Hazard Evaluations and Field Studies, Industrywide Studies Branch, Cincinnati, OH 45226; and [B]Department of Family and Community Medicine, University of Massachusetts Medical Center, Worcester, MA 01605

A method has been developed for determining the quantity of the epoxide functional group in pure epoxy resins, resins in partially-cured mixtures with amine curing agents, and commercial epoxy surface coatings. The method is based upon the reaction of the epoxide group with bromide in the presence of acid, with measurement of excess bromide in the reaction mixture by normal pulse polarography. The method extends the range of previously reported methods for epoxy analysis to samples containing 1 to 100 microequivalents (μeq) of epoxide functionality, while maintaining good precision and accuracy (coefficient of variation <0.06; accuracy within 2% of expected). The method has been developed for application to analysis of the epoxy content of environmental aerosols such as those of epoxy paint sprays.

Introduction

Most epoxy surface coatings are based upon diglycidyl ether resins derived from epichlorohydrin and bisphenol A. These resins form surface coating films by chain extending and cross-linking reactions of terminal epoxide groups with curing agents such as amines. A small proportion of the epoxy surface coatings are based upon modified epoxy resins (epoxy esters) that do not contain reactive epoxy groups; however, the vast majority of epoxy paints contain unmodified (reactive) epoxy resins with average molecular weights of 400 to 4000 g/M. These paints are used to form protective coatings with good corrosion and chemical resistance, toughness and adhesion. They are used as coatings for containers such as food and beverage cans, high performance coatings for aircraft, transportation and construction equipment, and marine coatings.

A painter applying an epoxy paint may be exposed to an aerosol containing a reactive mixture of epoxy resin and curing agents which has begun to polymerize, as well as solvents, diluents and pigments. Conventional industrial hygiene methods that evaluate aerosol exposures based upon mass or count concentration do not provide useful information about the reactive epoxy content of the aerosol. The potential health effects of contact with epoxy compounds in surface coatings are not known with certainty; however, a wide range of effects has been reported in human and animal studies of epoxy compounds.(1) These effects are probably the result of the epoxide functional group reacting with proteins and other nucleophilic substances. A sampling and analytical method has been developed to collect epoxy-containing aerosols, stop the reaction between the epoxy and curing agent, and measure the unreacted epoxide content of the aerosol as it existed at the point of human exposure. This paper describes the development of the analytical method. The application of the method to aerosol sampling and to analysis is the subject of the second paper in this series.

Characteristics of Epoxy Compounds

The terms epoxy and epoxide generally are applied to compounds containing oxirane rings. The oxirane (three-membered cyclic ether) groups are much more reactive than open chain ethers because of the strain created by the carbon-oxygen bond angles, which are approximately 60 degrees in the cyclic ethers, compared to 110 degrees in open chain ethers. The epoxide ring is opened easily by a variety of nucleophilic agents, making the epoxides very reactive compounds. This reactivity has caused epoxides to be used widely in commercial and industrial applications. The simplest epoxide, ethylene oxide, is used as a fumigant, medical sterilant and chemical intermediate. Epoxy resins, most of which are oligomers of the epichlorohydrin-bisphenol A type resin molecule shown in Figure 1, are products of considerable commercial significance, with a 1980 domestic production of 143 000 metric tons (315 million pounds).(2) Approximately 45% of the total production of epoxy resins is used in epoxy protective coatings. These surface coatings are applied as reactive mixtures of epoxy resins, curing agents and a variety of possible solvents, pigments and fillers. When a painter applies an unmodified epoxy paint by common spray painting techniques, the paint droplets contain epoxy resin molecules that have begun to form a polymer by chain-extending and cross-linking reactions with the curing agent. At the time of application, the degree of conversion of the resin is quite low; that is, most of the

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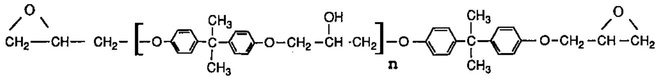

Figure 1 — Model epoxy resin molecule.

epoxide functional groups have not yet undergone reaction. The epoxy paint cures to its final polymeric structure after several hours of air drying or elevated temperature baking. Since the curing reactions continue to change the chemical properties of the aerosol after deposition on a surface or on a sampling device such as a filter, estimation of reactive epoxide exposure is a difficult task.

Approximately 15% of the epoxy surface coatings contain modified epoxy resins. Modified epoxy resins (epoxy resin esters) are derivatives of epoxy resins that have been converted to esters by reaction with fatty acids, rosin acid or tall oil. The modified epoxy resins do not contain unreacted epoxide groups; however, they are still referred to as epoxy coatings. Since the analytical method has been developed to measure the reactive epoxide content of surface coatings, it is not applicable to coatings based upon modified epoxy resins.

Existing Methods for Epoxide Analysis

The reactivity of the epoxide group has been the basis for many methods for measuring content of solid and liquid resins;$^{(3)}$ an early air sampling method for ethylene oxide was based upon the hydrolysis and oxidation of ethylene oxide.$^{(4)}$ Most chemical methods for measurement of epoxide content of resins are derived from the epoxide ring-opening reaction with a halogen acid such as hydrochloric or hydrobromic acid. The most thoroughly documented analytical method$^{(5)}$ is American Society for Testing Materials (ASTM) Standard Test Method for Epoxy Content of Epoxy Resins (ASTM 1652-73). The principle of this method is the stoichiometric reaction of the epoxy groups with HBr to form bromohydrins (Figure 2). The quantity of acid (hydrogen ion) consumed by this reaction (*i.e.,* 1 g equivalent, or M, of H^+ reacts with 1 g equivalent, or mol, or epoxide) is a measure of the epoxide content of the resin. According to the nomenclature used in ASTM Method 1652-73, the epoxide content of a sample is reported as the number of gram equivalents of epoxy groups per 100 grams of resin, or the weight per equivalent is reported as the mass of sample containing one gram equivalent of epoxy groups.

The ASTM method, and other methods based upon change in pH, cannot be applied to mixtures of epoxy resins and the commonly used curing agents such as amines, because amines will themselves change the pH. The interference caused by acidic or basic curing agents can be avoided by measuring the consumption of anion (bromide or chloride) by the epoxy ring-opening reaction to provide a measure of epoxide content. Methods based on anion consumption also have been used to measure the epoxy content of partially-cured resins, allowing determination of the degree of cure.$^{(6)}$ To maintain consistency with the nomenclature of ASTM Method 1652-73, sample epoxy content is reported as the mass of sample (grams) found to consume 1 g equivalent of bromide ion.

The stoichiometric hydrobromination of epoxide by bromide generated *in-situ* from tetraethylammonium bromide (TEAB) has been identified as the most promising chemical method for epoxide analysis.$^{(3)}$ This approach has been used by several investigators to measure the epoxy content of pure and partially-cured epoxy resins. These methods are summarized in Table I. By using dilute perchloric acid to titrate epoxy samples dissolved in glacial acetic acid containing excess TEAB, analysis of pure epoxy resin in 5 mg samples containing as little as 0.03 milliequivalent (meq) of epoxide has been reported by Selig.$^{(7)}$ The minimum amount of reactive epoxide that can be measured by direct titrimetric methods is limited by the speed of the hydrobromination reaction, which is very slow at low epoxide concentrations, resulting in indistinct endpoints.$^{(8)}$ For mixtures of epoxy resins and amine curing agents, Selig and Crossman$^{(6)}$ found that the greatest sensitivity was achieved by reacting samples with a two-fold molar excess of bromide generated *in-situ*, and measuring residual bromide after the hydrobromination reaction was completed. By using this method, the epoxide content of pure and partially-cured resins was measured in 200 mg samples containing 1 meq of epoxide.$^{(6)}$ In order to develop a method applicable to the measurement of the epoxy content of aerosols, the principle of hydrobromination with excess bromide and measurement of the unreacted bromide in the reaction mixture has been applied, and the range of the method has been extended to measure smaller quantities of epoxide than previously reported.

Experimental

Measurement of Total Epoxide Reactivity

For the development and evaluation of the analytical method, diglycidyl ether of bisphenol A (DGBA), a difunctional epoxy resin with a molecular weight of 340 g/M (170 g/epoxide equivalent) was used as a model compound. The resins used in commercial surface coatings are usually mixtures containing DGBA and higher molecular weight homologues of DGBA. Use of a model compound of known epoxide content allowed evaluation of the method's ability

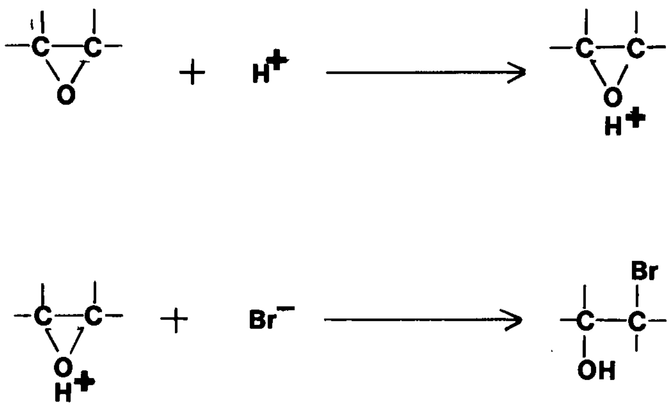

Figure 2 — Hydrobromination reaction of the epoxide group.

TABLE I
Some Existing Methods for Epoxy Analysis

Method	Principle	Sample Size
ASTM 1965-73(5)	Direct titration with HBr, colorimetric endpoint.	1 meq (170 mg DGBA)
Selig and Crossman(6)	Br generated *in situ*, titration of excess Br, Br selective electrode.	1 meq (170 mg DGBA)
Selig(7)	Br generated by titration with $HClO^{1}$, potentiometric endpoint.	0.03 meq (5 mg DGBA)

to measure the epoxy content of samples by comparison with the theoretical value for the pure compound and measurements made with independent methods. Since the analytical method determines the total reactive epoxy content — regardless of the identity of the specific molecules to which the epoxide groups are attached — the method is equally applicable to pure compounds (such as the model DGBA), resin mixtures found in commercial epoxy surface coatings, and partially-cured mixtures of resins and curing agents. During the development and evaluation of the analytical method, the objectives were to establish the method's ability to measure the epoxy content of pure and partially-cured epoxy compounds, and to determine the method's potential applicability to aerosols containing commercial epoxy resins and surface coatings.

Reaction Conditions

The first step in the development of the analytical method was the selection of an appropriate reaction medium. Selection was based upon the following criteria:

1) The medium must be capable of solubilizing the epoxy in the sample, and swelling partially-cured resins to allow the hydrobromination reagent to contact all reactive epoxide groups;
2) The medium must not itself react with the epoxide or the reagent, or interfere with the measurement of residual bromide concentration;
3) The medium must inhibit the reaction between the epoxy and the curing agent; and
4) The medium must be compatible with samples collected by a personal air sampling device.

Eighteen compounds with good solvent properties for epoxides (including dioxane, chloroform, toluene, acetic acid, and several phthalates and glycol ethers) were evaluated, and dimethyl formamide (DMF) was found to be the medium that best satisfied these criteria. The analytical method that has been developed is based upon the hydrobromination of epoxide in DMF, with measurement of the excess bromide in the reaction mixture by normal pulse polarography (NPP).

The method was applied to measure the epoxy content of two pure epoxy compounds, butyl glycidyl ether and DGBA. The epoxy content of several commercial epoxy resins, and epoxy surface coatings also was determined, and the method was applied to mixtures of epoxy resins and curing agents. To determine the epoxy content of pure or partially-cured epoxy resins, samples containing 1 to 100 μeq epoxide (0.17 to 17 mg DGBA) were dissolved in DMF (ACS Certified, Fisher Scientific). The volume of DMF used to dissolve the sample was adjusted to maintain a minimum epoxide concentration of approximately 0.3 meq/L in the reaction mixture. For example, the volume of the reaction mixture for samples containing 0.17 mg of DGBA was approximately 3 mL; larger DGBA samples were dissolved in 5 to 10 mL DMF. For bulk samples of unknown epoxide content, a working solution was prepared by accurately adding 1.0 g of the material to 10 mL of DMF; aliquots of this solution were diluted in DMF and a series of reaction mixtures was prepared over a 10- to 1000-fold range of dilutions of the working solution. Partially-cured resin samples that had hardened during the latter stages of curing were reduced to smaller particle sizes by grinding in a vibratory ball mill. The fraction of ground resin that passed a No. 140 standard seive (less than 105 μm diameter) was suspended in DMF, which swelled the polymer lattice to allow the hydrobromination reagent to diffuse into the partially-cured resin and react with residual epoxy groups.(9)

Tetraethylammonium bromide (TEAB, Fisher reagent grade, recrystallized from absolute ethanol) was dissolved in glacial acetic acid to create a solution approximately 0.05M in bromide. Aliquots of this solution accurately were added to create approximately a 3:1 molar excess of bromide to the estimated epoxide in the DMF, and concentrated perchloric acid ($HClO_4$) was added in a 10:1 molar excess to epoxide. This reaction mixture, containing the epoxide sample, TEAB and $HClO_4$ in the DMF was tightly capped and maintained in the dark for 4 hr at room temperature (22° C). Under these conditions, the hydrobromination reaction was found to be essentially complete (at least 90% recovery of expected epoxide) for samples with epoxy solution concentrations of at least 0.3 meq/L (approximately 1 μeq epoxide in a 3 mL sample volume). Residual bromide from the hydrobromination reaction was determined by NPP directly in the reaction mixture, or after dilution with DMF to a bromide concentration of approximately 1 mM. The quantity of epoxide in the sample, in terms of the reactive epoxide content, was determined from the difference between the molar quantity of bromide added and the quantity of residual bromide measured after the hydrobromination reaction had gone to completion.(6)

Polarography

Normal pulse polarography (NPP) was used to measure the concentration of bromide in the reaction mixture. Under the polarographic conditions described in Table II, chloride, bromide and iodide depolarize the dropping mercury electrode (DME) and give two anodic waves.(10) The limiting current of the first wave in the normal pulse mode is controlled by the diffusion of halide ions; therefore, the limiting current is linearly dependent upon halide concentration from 0.01 to 1.5 mM.(11,12) Bromide concentration in the reaction mixture was determined by measuring the limiting current at a pulse potential of -0.02 V, and comparison with bromide standards of TEAB in 0.1 N tetraethylammonium

TABLE II
Polarographic Conditions[A]

Polarograph:	Princeton Applied Research Model 174A with PAR Drop Timer 174/70.
Electrode:	Dropping mercury electrode; 0.5 sec drop time.
Reference Electrode:	Saturated Calomel Electrode (SCE) connected through liquid junction.
Auxiliary Electrode:	Platinum wire.
Supporting Electrolyte:	Tetraethylammonium perchlorate (TEAP) in DMF (0.1M).
Operating Conditions:	Initial potential -0.5V; scanning in the positive direction at 2mV/s to +0.35V.

[A]Adapted from Matsui(10) and Wojciechowski and Osteryoung.(11,12)

perchlorate (TEAP)/DMF analyzed under the same polarographic conditions.

Epoxy — Curing Agent Mixtures

The test method's ability to measure the epoxy content of partially-cured epoxy/polyfunctional amine curing agent mixtures was evaluated using a model system of butyl glycidyl ether (BGE) and diethyl amine (DEA). Ethanol and DMF were both tested as solvents for the reaction mixtures, which were 1M in BGE and DEA. As the epoxy/amine curing reaction proceeded at 22°C, samples containing approximately 10 μeq unreacted epoxy were taken consecutively for measurement of epoxy conversion. The curing reactions of several commercial epoxy resin/curing agent systems also were studied by measuring the change in epoxide content as the curing reaction proceeded.

Potential Interferences

Two sources of potential interference in the measurement of epoxide content have been evaluated in this method development. Since the method is based upon the stoichiometric consumption of bromide ion by the epoxide hydrobromination reaction, other bromide-consuming reactions will provide a positive interference, resulting in the overestimation of epoxide content. The effect of compounds likely to be present in epoxy surface coatings — such as mineral spirits, glycol ethers, aromatic hydrocarbons, ketones, formaldehyde, water and titanium dioxide — was determined by preparing a series of epoxy resin samples — each containing approximately 0.5 mg DGBA in DMF. Each sample contained up to 10% (by weight) of one of these potentially interfering compounds. The epoxy content of each sample was measured and the effect of these compounds on recovery of DGBA was determined.

The other source of possible interference is in the polarographic measurement of unreacted bromide concentration in the reaction mixture. When NPP is applied to this measurement in hydrobromination reaction mixtures, the samples contain small amounts of the bromohydrin produced from the epoxy, acetic acid (the solvent for TEAB), and perchloric acid, in addition to the TEAP supporting electrolyte. The effect of these compounds — and other likely constituents of epoxy surface coatings — on the polarographic waves used to determine bromide concentration was evaluated.

Results and Discussions

Uncured Epoxy Compounds

The first step in the development and evaluation of the method was its application to the measurement of the epoxide content of pure epoxy compounds. Table III compares the theoretical epoxide equivalent weights of a monofunctional epoxide, butyl glycidyl ether, and DGBA with measurements made by ASTM Method 1652-73 and the test method. Results are reported as the epoxide equivalent

TABLE III
Epoxy Content of Model Compounds[A]

Compound	Sample Mass (mg)	Experimental Equivalent Weight (g/eq)		Theoretical Epoxide Equivalent Weight (g/eq)
		ASTM 1652-73	Test Method	
BGE[B]	120.04	131.98(1.77)		130.21
	0.13		130.79(6.71)	
DGBA[C]	170.11	173.32(0.82)		170.23
	16.62		169.34(0.45)	
	1.80		174.64(3.29)	
	0.17		172.47(2.40)	

[A]Experimental equivalent weights reported as the mean of six replications, with sample standard deviations reported in parentheses.
[B]Butyl Glycidyl Ether.
[C]Digylcidyl Ether of Bisphenol A.

weight, which is the mass of epoxy compound containing 1-gram equivalent of epoxide functional groups. Measurements of epoxide content made from 1 to 100 μeq (0.17 to 17 mg DGBA) by the test method were within 2% agreement with the theoretical values for pure compounds and the measurements made using ASTM Method 1652-73; the precision (coefficient of variation) did not exceed 0.06. The test method is capable of measuring epoxy content over a wide range of sample sizes and is applicable to samples containing as little as 1 μeq epoxide. The smallest quantity of epoxide that could be detected by the test method was limited by the minimum concentration of epoxide that reacted quantitatively with bromide in the reaction mixture. At epoxide solution concentrations below 0.3 meq/L (1 μeq epoxide in 3 mL solution), the hydrobromination reaction converted less than 90% of the epoxide to bromohydrin, resulting in low recoveries. The reaction mixture was maintained at room temperature (22° C) and kept from direct sunlight to prevent bromide-consuming side reactions, such as the oxidation of bromide to bromate by perchloric acid.

The method also was applied to several uncured commercial epoxy resins and surface coatings. The results of these measurements are presented in Table IV. These measurements were made on samples containing approximately 1 μeq epoxide and are in close agreement with product specifications and measurements made by the ASTM method. The ASTM method could not be applied to pigmented surface coatings, since the color of the sample obscured the colorimetric endpoint.

Polarography

Figure 3 presents the NPP waves obtained for solutions of TEAB (0.25 to 1.35 mM) in 0.1M TEAP/DMF. These waves were consistent with those reported previously,(10) with the half wave potential (E 1/2) for the more negative wave of TEAB in this concentration range to be approximately -0.14 V *vs.* the saturated calomel electrode (SCE). Based upon examination of the first wave, -0.02 V was selected as the pulse potential at which measurements of limiting current were made. There was a strong linear relationship between bromide concentration up to 2.9 mM and limiting current measured in this concentration range (r = 0.99).

Epoxy-Curing Agent Mixtures

Mixtures of BGE (the model epoxy compound) and DEA were used to evaluate the test method's ability to measure the epoxide content of partially-cured epoxide/curing agent mixtures and to confirm the reported inhibition of the curing reactions by DMF.(13) The curing curves for mixtures of BGE and DEA are presented in Figure 4. The inhibition of the curing reaction by DMF and the acceleration by ethanol were observed, as previously reported.(13,14) The degree of epoxide conversion in DMF at 24 (13.2%) and 48 hr (17.2%) agreed well with other curing studies,(15) which reported that equimolar mixtures of phenyl glycidyl ether and DEA in DMF at 25° C, showed 12.9% of the epoxide reacted in 24 hr, with 24.3% conversion in 48 hr.

TABLE IV
Epoxy Content of Commercial Materials

Compound	Sample Mass (mg)	Experimental Equivalent Weight (g/eq)[A]		Specified Epoxide Equivalence (g/eq)
		ASTM 1652-73	Test Method	
DER 332[B]	170.41	178.02(2.31)		172-176
	0.17		179.29(1.99)	
DER 324[C]	190.20	207.86(0.29)		195-213
	0.23		202.13(3.72)	
DEN 431[D]	170.97	182.76(1.00)		172-179
	0.18		176.58(2.45)	
A[E]	0.88		1175.0 (48.6)	
B[F]	0.16		236.97(7.36)	
C[G]	1.68		2315.3 (43.5)	

[A] All experimental equivalent weights reported as the mean of six replications, with sample standard deviations reported in parentheses.

[B] Compound A is Tile-Like Catalyzed Architectural Coating, High Gloss Enamel Base, Light 371 90 from Benjamin Moore and Company. The vehicle is specified to be 62.8% nonvolatile epoxy resin solution.

[C] Compound B is EnviroTex 1 to 1 Polymer Coating, from Environmental Technology Inc. The resin is specified as an epoxy bisphenol A resin.

[D] Compound C is Klenk's Epoxy Enamel Tub and Tile Finish, White-8151, from Zynolyte Products, Inc. The vehicle is described as 97% epoxy by weight.

[E] Dow Epoxy Resin 332 is a pure DGBA resin.

[F] Dow Epoxy Resin 324 is a mixture of liquid DGBA resin and C_{12} to C_{14} alkyl glycidyl ethers.

[G] Dow Epoxy Novolac is a polygylcidyl ether of phenol-formaldehyde novolac.

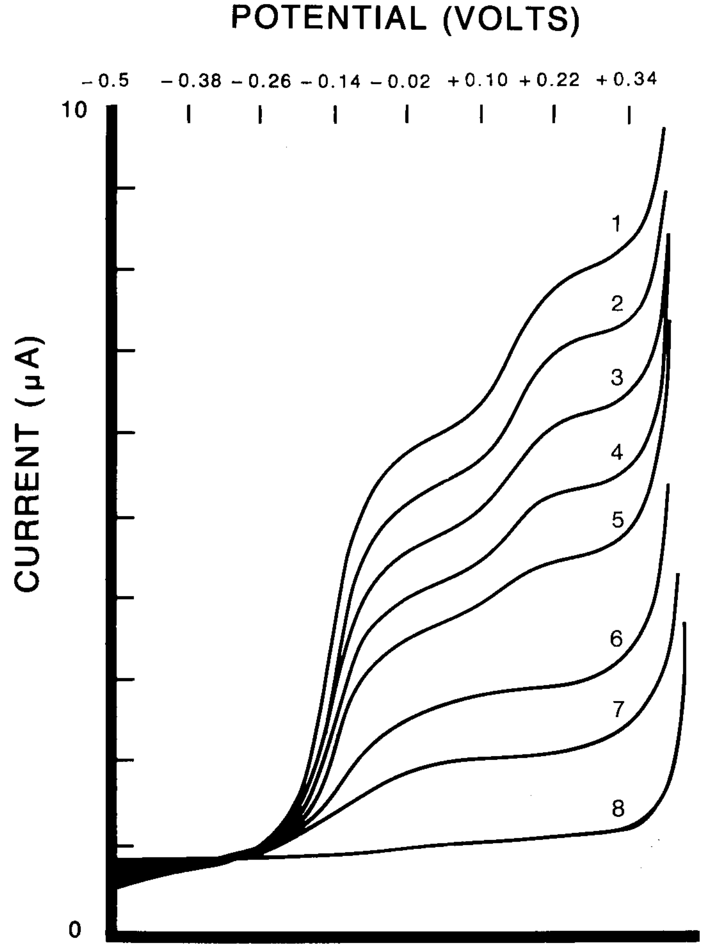

Figure 3 — NPP Waves of TEAB in 0.1N TEAP/DMF: Curve 1, 1.35 mM Br−; 2, 1.20 mM; 3, 1.02 mM; 4, 0.85 mM; 5, 0.69 mM; 6, 0.42 mM; 7, 0.25 mM; 8, Blank.

The curing reactions of several commercial epoxy resin/curing agent systems also were studied using the test method. Figure 5 shows the curing curves for a 2:1 mixture of DER 330 (a Dow DGBA-type resin) with Versamid 125 (a polyamine curing agent, Henkel Corporation), Envirotex Polymer Coating, and Tile-Like Catalyzed Architectural Coating (Benjamin Moore and Company). These curing curves are similar to those reported using other methods to evaluate the amine curing reactions of DGBA-type epoxides.(6,16)

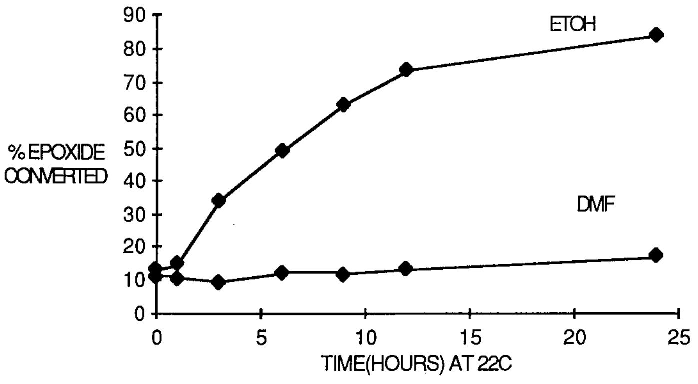

Figure 4 — Curing curves for 1M mixtures of BGE and DEA in ETOH and DMF.

Potential Interferences

Interference caused by the consumption of bromide ion by compounds other than epoxide in the reaction mixture was evaluated by preparing a series of solutions containing 10% (by weight) of mineral spirits, toluene, methyl ethyl ketone, cellosolve (2-ethoxyethanol), formaldehyde (as a formalin solution) and titanium dioxide in DMF. Each sample was spiked with DGBA at approximately three times the minimum detectable quantity (0.5 mg), and TEAB and perchloric acid were added to initiate the hydrobromination reaction. Recovery of the expected epoxide was within 10% of that expected in each case.

The effect of acetic and perchloric acids on the polarographic waves for bromide was evaluated by adding these materials to solutions of TEAB in 0.1M TEAP (supporting electrolyte) in DMF. These compounds did not have a significant effect on the shape of the polarographic waves or the linearity of the limiting current to bromide concentration relationship (Table V). The effect of other materials found in epoxy surface coatings — including toluene, ketones, glycol ethers and polyfunctional amines — on the polarographic waves also was investigated and no effect was observed on the first polarographic wave in solutions containing up to 10% (by weight) of these materials. The second wave, however, was disrupted by amines, probably because of formation of a mercuramine complex, or interference with the reaction of the HgX_3 monolayer that is adsorbed on the DME by the electrochemical processes responsible for the first wave. This monolayer is necessary for the formation of the second wave.(12) Since the limiting current of the first wave is used to measure bromide concentration in the reaction mixture, the method is still applicable to partially-cured samples containing amine curing agents.

Conclusions

The application of NPP to the measurement of residual bromide in epoxy hydrobromination reaction mixtures provides a simple, accurate method for measuring the epoxy content of samples containing as little as 1 μeq epoxide. The presence of amines does not interfere with the method, allowing the determination of epoxy content in partially-cured resins. Constituents of commercial epoxy systems (such as toluene, aliphatic ketones, and glycol ethers) do not

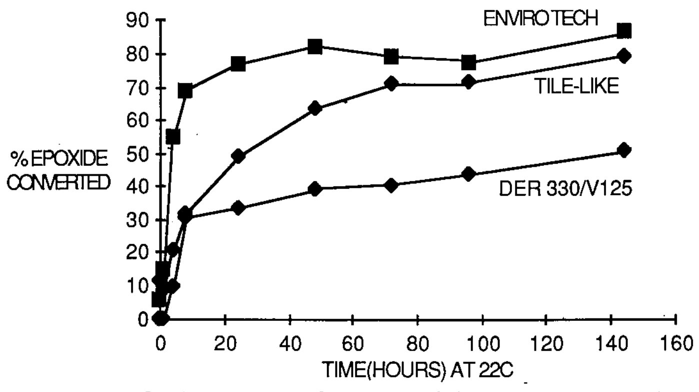

Figure 5 — Curing curves of commercial epoxy compounds.

TABLE V
Influence of Supporting Electrolyte on Bromide Concentration: Limiting Current Relationship

Supporting Electrolyte[A]	Bromide Conc. Range (meq/L)	Concentration: Log Limiting Current Plot Characteristics		
		Slope	y-Intercept	Correlation(r)
0.1M TEAP/DMF[B]	0.70-2.9	0.99 (0.91-1.06)	3.65 (3.46-3.84)	0.99
2.0M HOAc[C]	0.60-2.5	1.03 (0.92-1.15)	3.73 (3.41-4.05)	0.99
2.0M HOAc + 0.25M $HClO_4$[D]	0.60-2.5	0.96 (0.78-1.14)	3.53 (3.03-4.03)	0.99

[A] All solutions were 0.1M in TEAP. Results are reported with 95% confidence intervals in parentheses.

[B] Tetraethyl ammonium perchlorate in dimethyl formamide.

[C] Acetic Acid.

[D] Perchloric Acid.

interfere with the polarographic measurement of residual bromide concentration or the precision and accuracy of the measurement of epoxy content. Dimethyl formamide is an excellent solvent for DGBA-based resins; it also inhibits the epoxy-amine curing reaction and swells partially-cured resins, allowing the hydrobromination reagent to reach unreacted epoxide groups.

The test method meets the study objectives, extending the range of existing methods for epoxide analysis to samples containing as little as 1 μeq of epoxide in the presence of amine curing agents, while maintaining acceptable precision and accuracy (CV <0.06, accuracy withing 2% of expected). This represents an improvement over the minimum detectable quantity of pure epoxide (30 μeq/sample) previously reported,(7) and the 1 meq epoxide/sample measured in mixtures of epoxides with amine curing agents.(6) Throughout the development of this method for epoxy measurement, the applicability of the method to the collection and analysis of epoxy-containing aerosols has been a primary consideration. This application of the method to environmental aerosols is described in the second paper of this series.

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