

# Quaternary Phosphonium Compounds as Latent Accelerators for Anhydride-Cured Epoxy Resins.

## I. Latency and Cure Characteristics

J. D. B. SMITH, *Westinghouse R&D Center,  
Pittsburgh, Pennsylvania 15235*

### Synopsis

Quaternary phosphonium compounds have been found to be extremely effective latent accelerators for anhydride-cured bisphenol A epoxy resins; at concentrations from 0.01% to 0.25%, fast gel times are found in the temperature range of 135°–200°C combined with very good storage properties at ambient temperatures. Using these materials as accelerators, it is possible to formulate long-life, one-component epoxy resins. From gel time data, Arrhenius plots were made for some of these phosphonium compounds, and results indicate low activation energy values of the order of 16.1 kcal/mole. Reaction mechanisms are proposed to explain the effectiveness of these phosphonium compounds as latent accelerators. The initiation mechanism probably involves the formation of hydrogen-bonded phosphonium–epoxy or phosphonium–anhydride complexes which rearrange on the application of heat to form activated species resulting in polymerization of the epoxy–anhydride components. The transfer of a proton from the phosphonium complex(es) to other epoxy or anhydride molecules would appear to be the rate-determining step in this initiation mechanism. Comparison of other well-known accelerators used for the anhydride cure of bisphenol A epoxy resins shows quaternary phosphonium compounds to be among the most effective accelerators disclosed to date.

### INTRODUCTION

A considerable amount of effort has been devoted in recent years, mainly in the electrical industry, to develop a perfect latent catalyst for curing epoxy resins. This has been particularly the case in the manufacture of electrical equipment such as motors, transformers, and generators, where epoxy resins are utilized in such diverse processes as casting, potting, encapsulation, and vacuum-pressure impregnation (VPI). For reasons of economy and convenience, it is normal practice to store “one-package” epoxy resins (i.e., catalyzed resins) in large storage tanks in close proximity to the processing area. Thus, adequate catalyzed storage stability at ambient combined with efficient reactivity and cure at elevated temperatures are necessary prerequisites.

The specific properties required by an ideal “latent” catalyst would be the following: (a) It should give rapid cure of epoxy resins at moderately elevated temperatures (i.e., 120°–180°C). (b) It should be completely miscible with the resins at all temperatures. This is particularly true of impregnating resins. (c) The storage life of the catalyzed resin should be indefinite. In practice, the viscosity of the resin should not change appreciably at room temperature over periods ranging from several months to years. (d) It should not adversely affect the properties of the cured resin (e.g., tensile and electrical properties).

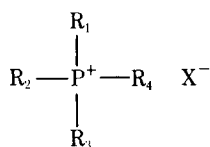
Numerous patents<sup>1–3</sup> have been issued in recent years on the development of latent catalysts for diglycidyl ether of bisphenol A resins (DGEBA), but most

fulfill only a few of the conditions outlined above. One of the most successful of these has been the boron trifluoride-monoethylamine complex<sup>4</sup> (BF<sub>3</sub>-MEA) BF<sub>3</sub>-400 (Harshaw Chemical Co. trademark). However, one of the serious disadvantages of this particular latent catalyst is the poor electrical properties at elevated temperatures of the epoxy resin in the cured state.<sup>5</sup>

To improve high-temperature stability over amine-cured systems and to give better physical and electrical properties above their heat distortion temperatures, it has been general practice in epoxy resin systems to use anhydride curing agents with DGEBA epoxy resins.<sup>6</sup> Most anhydride formulations require elevated-temperature cures with the ultimate properties dependent on postcures at temperatures of 150°C or higher.

For most commercial applications it is necessary to add some form of accelerator to the formulation to speed the rate of cure. Both acidic and basic accelerators can be used. Consequently, several latent accelerators have appeared on the commercial scene in recent years. Included among these are quaternary ammonium halides (such as benzyltrimethylammonium chloride<sup>7</sup>), stannous octoate,<sup>3</sup> zinc stearate,<sup>8</sup> "extra-coordinate" silicate salts,<sup>9</sup> triethanolamine borate,<sup>10</sup> triethanolamine titanate,<sup>11</sup> and various other metal chelates.<sup>12</sup> However, all of these materials have been rejected for one reason or another, and the quest for improved latent accelerators for anhydride-cured epoxy resins has continued.

Recent work<sup>13</sup> in our laboratories has revealed a new family of latent accelerators. This new family of compounds is derived from the salts of tertiary organophosphines and aryl or alkyl halides which have the general structural formula



where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are alkyl or aryl groups and X<sup>-</sup> is halogen, acetate, or dimethyl phosphate anion.

Most of the data reported here will be concerned with bisphenol A epoxy resin systems cured with the liquid anhydride 1-methyltetrahydrophthalic anhydride (the Union Carbide commercial designation for this material is ZZLA-0334). However, these quaternary phosphonium compounds have also been shown to be effective with other anhydrides such as hexahydrophthalic anhydride (HHPA).

## EXPERIMENTAL

Seven different quaternary phosphonium salts were evaluated in this work: (i) methyltrioctylphosphonium dimethyl phosphate (MTO-P-DMP), (ii) tetrabutylphosphonium acetate (TBPA), (iii) methyltributylphosphonium dimethyl phosphate (MTBP-DMP), (iv) benzyltriphenylphosphonium chloride (BTTPC), (v) tetrabutylphosphonium chloride (TBPC), (vi) methyltriphenylphosphonium dimethyl phosphate (MTPP-DMP), and (vii) triphenylethylphosphonium iodide (TPEPI).

With the exception of TPEPI, supplied by Arapahoe Chemical Company, Boulder, Colorado, all of the phosphonium compounds were supplied by Cincinnati Milacron, Reading, Ohio.

Most of the evaluation studies were made using a 1:1 stoichiometric bisphenol A epoxy-anhydride formulation. The various quaternary phosphonium compounds were added at a 0.01%–0.25% level (based on the combined anhydride and epoxy resin weights). With the exception of MTPP-DMP, which showed partial insolubility in the resin formulation, excellent solubilities at ambient temperature were found.

### Gel Time Data

Initially, gel times were recorded on 10-g samples of resin in 2-in.-diameter aluminum dishes over the temperature range of 135°–170°C. Later, to give improved accuracy, the gel time measurements were made in 19 × 150 mm test tubes in a constant-temperature silicone oil bath using a Sunshine gel meter.

### Storage Stability Data

Storage stability characteristics of the formulations were followed at room temperature (i.e., 25°C) using a Gardner–Holdt bubble viscometer (ASTM D154-56). Termination of a sample's catalyzed lifetime (i.e., storage life) was taken to be when the viscosity reached a value of 1000 cps at 25°C.

## RESULTS

The data shown in Figures 1 and 2 indicate the effectiveness of two of the phosphonium compounds as accelerators for the epoxy-anhydride resin. Figure 1 gives "gel time" data as a function of temperature and accelerator concentration for the methyltrioctylphosphonium dimethylphosphate (MTOP-DMP) compound, whereas Figure 2 shows similar data obtained with tetrabutylphosphonium acetate (TBPA). It is noted that fast gel times (i.e., < 60 min) can be obtained with small amounts of accelerator (e.g., 0.06%), particularly at temperatures above 150°C. In the absence of accelerator the epoxy-anhydride resin shows very sluggish curing properties, the gel time at 150°C being in excess of 10 hr. In Figures 3–5, typical viscosity-versus-storage time curves are presented for the MTOP-DMP, MTBP-DMP, and TBPA phosphonium compounds, respectively. It is noted that "families" of curves can be constructed for each accelerator at their different concentrations. As might be anticipated, the viscosity changes become more rapid as the accelerator concentration increases.

However, appreciable latency is shown by these phosphonium compounds as demonstrated by the storage data shown in Table I. Using 1000 cps (at 25°C) as being the limiting viscosity, "storage lifetime" values can be assigned to each of the phosphonium compounds as indicated in Table I. It would appear that the nonhalide phosphonium compounds (e.g., MTOP-DMP and MTBP-DMP) exhibit higher latency than those containing halides. These differences may be linked to the presence of impurities or hydrolyzed byproducts in the halide compounds. In this respect it was noted that two of the materials investigated (i.e., BTPPC and TBPC) had pungent odors suggesting the presence of free organophosphine, presumably resulting from sample degradation or hydrolysis.

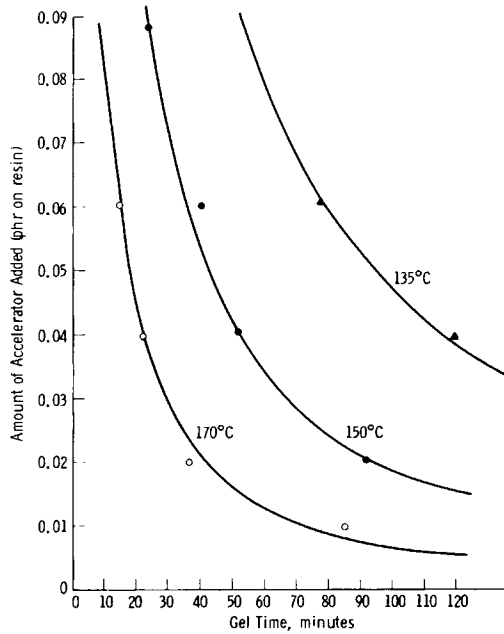


Fig. 1. Gel time data for epoxy-anhydride resin with MTOP-DMP accelerator (methyltrioctylphosphonium dimethyl phosphate).

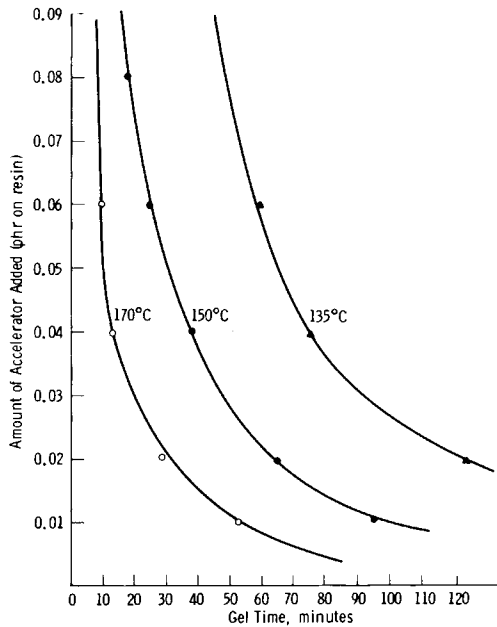


Fig. 2. Gel time data for epoxy-anhydride resin with TBPA accelerator (tetrabutylphosphonium acetate).

The three phosphonium compounds showing the best compromise between storage lifetime and catalytic effectiveness were MTOP-DMP, MTBP-DMP, and TBPA.

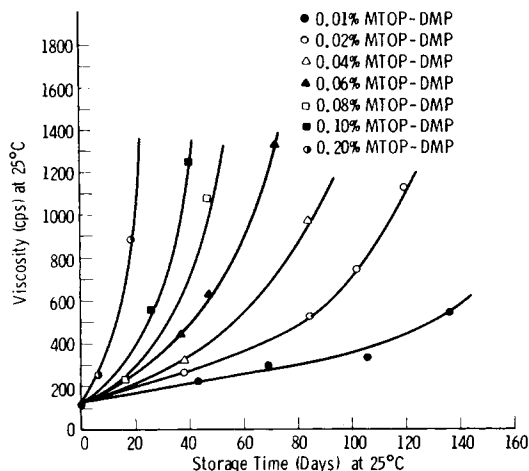


Fig. 3. Storage characteristics of epoxy-anhydride impregnant with different concentrations of MTOP-DMP (methyltriethylphosphonium dimethyl phosphate).

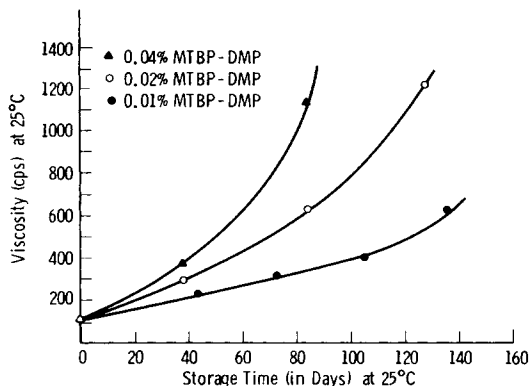


Fig. 4. Storage characteristics of epoxy-anhydride impregnant with different concentrations of MTBP-DMP (methyltributylphosphonium dimethyl phosphate).

In order to shed some light on the role of these quaternary phosphonium compounds in epoxy-anhydride systems, additional gel time data were obtained with the MTOP-DMP accelerator over the temperature range of 150°–200°C, using the constant-temperature bath and the Sunshine gel meter as mentioned previously. Relative reaction rate values could then be obtained at each temperature as shown in Table II for MTOP-DMP at a concentration of 0.04%.

In these calculations it was empirically assumed that the extent of reaction to the gel point was 50% so that the “relative reaction rate” is given by 50/gel time (in %/min).

This assumption may not be completely valid since the various crosslinking reactions in this resin system (e.g., etherification and esterification) may not vary uniformly with temperature (i.e., some crosslinks may be preferentially formed at the higher temperatures). However, this treatment does give an interesting insight into the role of quaternary phosphonium compounds in these systems. In Figure 6, an Arrhenius plot is shown for the data computed in Table II for the MTOP-DMP accelerator at 0.04% concentration. It is noted that a good linear

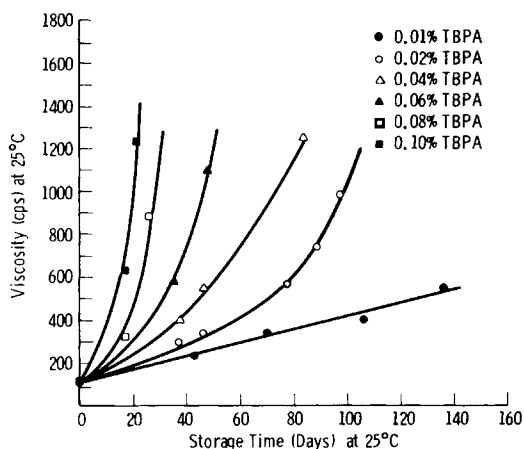


Fig. 5. Storage characteristics of epoxy-anhydride impregnant with different concentrations of TBPA (tetrabutylphosphonium acetate).

plot is obtained over the temperature range of 150°–200°C. From the slope of this plot an activation energy value of 16.1 kcal/mole is obtained.

This type of evaluation was then repeated for the MTOP-DMP and TBPA accelerators at higher concentrations in the resin (i.e., 0.25%). The gel time data

TABLE I  
Storage Lifetime Data for the Quaternary Phosphonium Compounds with Epoxy-Anhydride Resin

Quaternary phosphonium compound used	Concentration in epoxy-anhydride resin, % w/w	Molar concentration, moles $\times 10^{-4}$ in 200 g resin	Storage lifetime at 25 °C, <sup>a</sup> days
Methyltrioctylphosphonium dimethyl phosphate (MTOP-DMP)	0.02	0.78	130
	0.04	1.56	85
	0.06	2.34	56
	0.10	3.90	45
Tetrabutylphosphonium acetate (TBPA)	0.02	1.06	112
	0.04	2.12	80
	0.06	3.18	42
	0.10	5.30	21
Methyltributylphosphonium dimethyl phosphate (MTBP-DMP)	0.01	0.59	160
	0.02	1.17	115
	0.04	2.34	85
Benzyltriphenylphosphonium chloride (BTPPC)	0.02	1.03	90
	0.10	5.15	28
Tetrabutylphosphonium chloride (TBPC)	0.02	1.36	90
	0.10	6.80	30
Methyltriphenylphosphonium dimethyl phosphate (MTPP-DMP) <sup>b</sup>	0.02	1.00	150
Triphenylethylphosphonium iodide (TPEPI)	0.02	0.96	85

<sup>a</sup> Number of days for viscosity to reach 1,000 cps at 25°C.

<sup>b</sup> Some insolubility in the resin detected with this material.

TABLE II  
Relative Reaction Rates at Different Temperatures of Epoxy-Anhydride Resin with 0.04%  
Methyltrioctylphosphonium Dimethyl Phosphate

Temperature, °C	Gel times, min	Average value, min	Relative reaction Rate, <sup>a</sup> %/min
150	51.1	51.6	0.968
	52.1		
170	19.1	19.2	2.62
	19.2		
180	13.4	13.3	3.76
	13.2		
190	9.3	9.3	5.37
	9.3		
200	6.9	6.9	7.25
	6.9		

<sup>a</sup> Assuming 50% reaction to gel point  $\therefore$  relative reaction rate = 50%/gel time, min =  $x$  %/min

were used to compute relative reaction rates as before, and the Arrhenius plots for the two accelerators are given in Figure 7. This time, nonlinear plots were found over the temperature range of 150°–175°C for both MTOP-DMP and TBPA. The indication is that at the higher concentration of these accelerators, a change in the relative rates of the initiation and crosslinking reaction mechanisms occurs as a consequence of the phosphonium compound taking a direct role in the crosslinking processes.

It should be emphasized again that, although the treatment outlined above results in “activation energy” values, the use of data obtained in this way is questionable in view of the uncertainty of the assumption made in deriving these values.

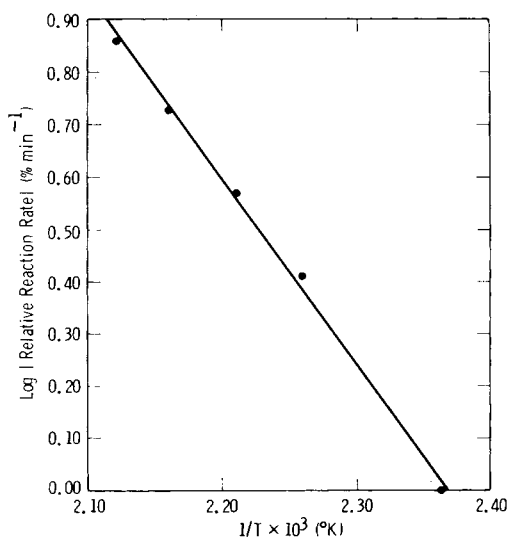


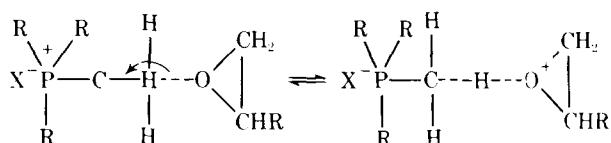
Fig. 6. Arrhenius plot for epoxy-anhydride resin gel time data (with 0.04% MTOP-DMP).



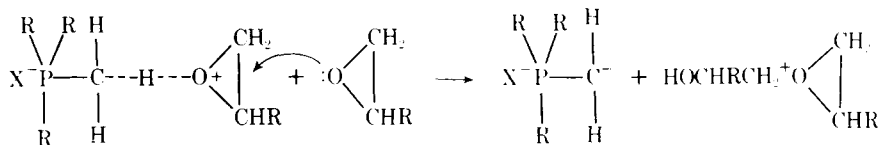


for the hydrogen atom. Since the amine is more basic, the hydrogen will normally be more strongly bonded to the nitrogen than to the oxygen. However, since the oxygen atom is contributing a portion of its electrons to the amine hydrogen atom, it will acquire a partial positive charge thereby causing a partial shift of electrons from an adjacent carbon atom as shown above. The curing mechanism at elevated temperature is then thought to proceed through an initiation mechanism resulting from the attack of nucleophile (such as an epoxy oxygen) on this complex to form oxonium ions, which are the propagating species in the subsequent polymerization.

A similar mechanism may take place in the accelerated polymerization of anhydride-cured epoxy resins with quaternary phosphonium compounds. In the case of a methyltrialkyl-type phosphonium salt, such as MTOP-DMP, the methyl ( $\text{CH}_3$ ) group attached to the phosphine phosphorus atom (P) would be expected to be fairly acidic in character (because of the close proximity of the empty  $d$ -orbitals of the phosphorus atom), and the acidic protons would be available for bonding with nucleophiles such as an epoxy oxygen. Thus,

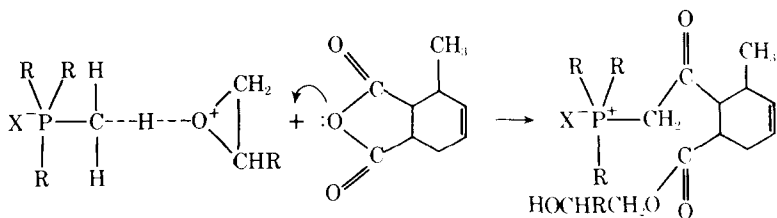


Although the quaternary phosphonium salt is written above as being ionic, it is now generally accepted that quaternary phosphonium compounds are more covalent in character than analogous quaternary ammonium compounds<sup>18</sup> (because of the close proximity of empty  $3d$  electron orbits in the phosphorus atom). The epoxy-phosphonium salt adduct would then be vulnerable to attack by another epoxy molecule resulting in the formation of an oxonium ion:



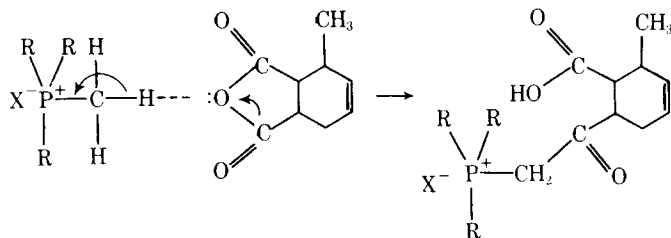
Mechanism I

During this reaction step, the electronic structure of the phosphorus atom will change from a  $sp^3d$  trigonal bipyramidal hybridization to a configuration closer to an octahedral  $sp^3d^2$  atom. It is a well known fact that phosphorus compounds, because of the presence of empty  $d$ -orbitals, can take up this octahedral configuration.<sup>19</sup> Also, reaction of this epoxy-phosphonium salt adduct with 1-methyltetrahydrophthalic anhydride is likely to form active hydroxy compounds:



Mechanism II

Direct reaction between the anhydride and quaternary phosphonium salt, however, is also a possibility:



Mechanism III

After the formation of carboxyl groups, direct epoxy-carboxylic acid reaction leading to polymerization will occur. All of these initiation reactions result in the formation of "active hydrogen" either in the form of carboxyl or hydroxyl groups. Once this occurs, then a normal epoxy-anhydride-type polymerization will proceed.<sup>20</sup> The homopolymerization of epoxy catalyzed by quaternary phosphonium salt (i.e., mechanism I) would probably proceed at a fairly sluggish pace but might become more significant at higher temperatures and at higher accelerator concentrations.<sup>21</sup> In the case of the tetraalkylphosphonium salts such as TBPA, the "active" hydrogen, which is removed by reaction with a nucleophile, is most likely to come from the  $\beta$ -carbon atom on the alkyl chain adjacent to the phosphorus atom. However, TBPA may be a special case since it contains one molecule of acetic acid per molecule of phosphonium salt as "water" of crystallization from its purification procedure. The role of the acetic acid may well be to supply "active" hydrogen to anhydride and epoxy.

The low activation energy value (i.e., 16.0 kcal/mole), computed from the data in Figure 6, would suggest that the rate-determining step in the initiation mechanism involves the dissociation of the phosphonium compound-epoxy or phosphonium compound-anhydride complexes to form the initiation species illustrated by mechanisms I, II, and III. This dissociation involves the breaking of a hydrogen bridge and the transfer of a proton to the epoxy or anhydride oxygen (i.e., the breaking of a low-energy bond occurs). Hydrogen bond strengths are known to vary anywhere from 8.0 up to 30.0 kcal/mole.

In this discussion the assumption has been made that the phosphonium compounds play a role only in the initiation mechanism and do not contribute significantly to the propagation rates. Although this might be true for low concentrations of phosphonium compound, it may not hold for higher values. The deviations from linearity noted in the Arrhenius plot shown in Figure 7 for the epoxy-anhydride resin with higher accelerator concentrations (0.25%) may be a consequence of the phosphonium compounds playing a significant role in the propagation rates (i.e., the phosphonium compounds are involved directly in the formation of crosslinks). However, in such a complex system as this, other explanations are also possible for these observed deviations.

To illustrate the effectiveness of these quaternary phosphonium salts as accelerators for anhydride-cured epoxy resins, a comparison of MTOP-DMP and TBPA with other well-known accelerators is given in Table III. The data were obtained from work done in this laboratory using the same resin system. To

TABLE III  
Relative Reactivities of Different Accelerators with Epoxy-Anhydride Resin at 150° and 135°C

Accelerator added to resin	Concentration in epoxy-anhydride resin		Gel time at 150°C, min	Gel time at 135°C, min	Relative reactivities of accelerators ( <i>R</i> ) ×	
	phr on resin	Moles × 10 <sup>-4</sup> in 200 g resin			150°C	135°C
MTOP-DMP (MW 510.7)	0.020	0.78	90	—	70.2	—
	0.060	2.34	—	80	—	187.3
TBPA (MW 378.4)	0.020	1.06	65	—	68.8	—
	0.060	3.18	—	60	—	190.1
Benzyltriethylammonium chloride (MW 227.8)	0.020	1.77	50	—	88.5	—
Benzyltrimethylammonium iodide (MW 277.2)	0.020	1.45	40	—	58.0	—
	0.100	7.22	12	30	86.6	216.0
1-Methylimidazole (MW 82.1)	0.063	15.22	12	23	183.0	350.0
2-Methylimidazole (MW 82.1)	0.063	15.22	—	17	—	259.0
Zinc stearate (MW 631.4)	2.500	79.20	—	40	—	3165.0
Zinc oleate (MW 627.4)	2.500	79.80	—	20	—	1592.0
N,N-Diethylethanolamine (MW 117.2)	0.025	4.27	50	—	—	213.5
Uranyl nitrate [UO <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> H <sub>2</sub> O] (MW 502.1)	0.020	0.80	20	—	16.0	—

<sup>a</sup> The quantity *R* is given by product of (gel time) × (accelerator concentration, in moles in 200 g resin).

make the comparison valid, the concentration given for each of these materials has been converted from "phr" to "moles/200 g resin." Thus, the comparison is made on a molecular concentration basis instead of weight. Gel times were recorded at 135° and 150°C as shown in Table III, and the measure of relative reactivity ( $R$ ) of each of the accelerators is given by the expression

$$R = (\text{time to reach gel point, in min}) \\ \times (\text{molar concentration of accelerator, in moles/200 mg resin})$$

Two sets of data have thus been calculated at 135° and 150°C and resolved: the *more reactive* the accelerator, the *lower* the product  $R$  will be.

Comparison of these data show quite clearly how much more reactive the phosphonium salts are in the resin system than compounds such as substituted imidazoles and organozinc salts (e.g., zinc stearate and octoate). The only accelerator that shows substantially more potency than the quaternary phosphonium salts is uranyl nitrate. However, this compound is not a latent accelerator in the sense that storage lifetimes are only of the order of a few days.

### References

1. I. N. Elbling and A. B. Finestone, Ger. Pat. 1,162,439 (to Westinghouse) (Nov. 1958).
2. L. F. Betnamont, Br. Pat. 869,969 (to Shell) (June 1961).
3. W. R. Proops and G. W. Fowler, Br. Pat. 966,917 (to Union Carbide) (Feb. 1965).
4. A. J. Landua, *ACS Div. Org. Coatings Plast. Chem. Prepr.*, **24** (2), 299 (Sept. 1964).
5. R. B. Feuchtbaum, *Insulation*, p. 47. (Sept. 1962).
6. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 5, p. 20.
7. W. J. Belanger, U.S. Pat. 2,928,807 (to Devoe and Reynolds Co.) (March 1960).
8. D. A. Rogers, Jr., and R. N. Kauffman, Westinghouse R&D unpublished work.
9. H. L. Vincent, C. L. Frye, and P. E. Oppliger, *Adv. Chem. Ser.*, **92**, 164 (1970).
10. S. H. Langer and I. N. Elbling, *Ind. Eng. Chem.*, **49**, 1113 (1957).
11. S. H. Langer, I. N. Elbling, A. B. Finestone, and W. R. Thomas, *J. Appl. Polym. Sci.*, **5**, 370 (1961).
12. Belg. Pat. 633,330 (to CIBA) (1963).
13. J. D. B. Smith, U.S. Pat. 3,784,583 (to Westinghouse) (Jan. 1974).
14. Reference 6, Chap. 9, p. 5
15. D. A. Rogers and J. D. B. Smith, U.S. Pat. 3,759,866 (to Westinghouse) (Sept. 1973).
16. C. K. Ingold, G. F. Fenton, L. Hey, and C. K. Ingold, *J. Chem. Soc.*, 989 (1933).
17. J. J. Harris and S. C. Temin, *J. Appl. Polym. Sci.*, **10**, 523 (1966).
18. G. M. Kosolapoff, *Organophosphorous Compounds*, Wiley, New York, 1950, Chap. 5, p. 78.
19. R. B. Heslop and P. L. Robinson, *Inorganic Chemistry*, Elsevier, Amsterdam-New York, 1960, Chap. 20, pp. 310-313.
20. Reference 6, Chap. 5, pp. 20-24.
21. J. D. B. Smith, Westinghouse R&D unpublished data.

Received November 3, 1977

Revised February 24, 1978