

The Chemistry of New Latent Curing Systems for Epoxy Resins

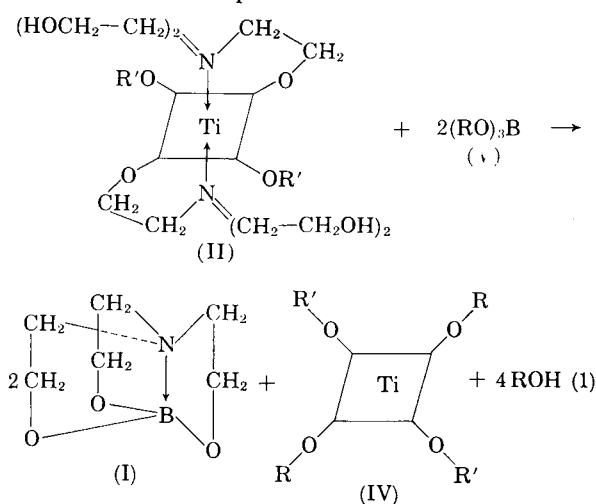
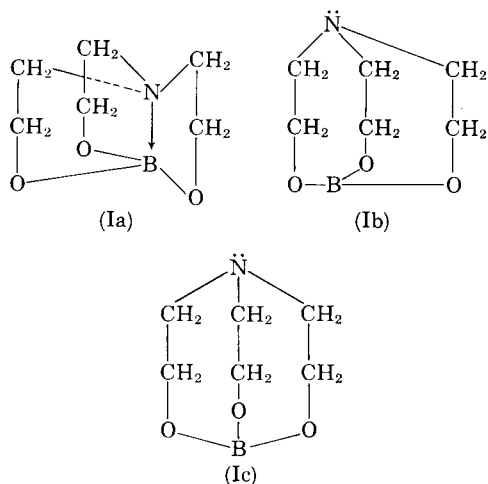
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The use of standard commercial epoxy resins—reaction products of bisphenol A and epichlorohydrin—frequently is limited and governed by the properties of the curing agent–resin mixtures as well as by the properties imparted to the hardened resin by the curing agent. In this article, we describe and illustrate how some of these properties may be altered and controlled through selection of curing agent components which eventually react to give triethanolamine borate^{1,2} and other reactive products. The basis for the selection and the application of triethanolamine borate (I) as a curing agent was discussed earlier.^{3,4} The primary consideration was the possibility that the internally coordinated “tryptych” structure (Ia) would dissociate at elevated temperatures to give (Ib) and/or (Ic), both of which contain a sterically unhindered electron pair efficient in nucleophilic attack⁵ and in catalytic curing of epoxy resin. Structure (Ic) would imply that the boron atom is out of the plane of the three oxygen atoms,

disturbing the “borate resonance,”⁶ and the vacant boron orbital is available for coordination and for assisting in epoxy ring cleavage.³

While triethanolamine borate (I) was reasonably soluble in most epoxy resins, its high melting point, 236–237.5°C., and slow rate of solution at room temperature made it necessary to pulverize and dissolve it with stirring at elevated temperatures of 50 to 90°C. Because of this, it was deemed desirable to form (I) in solution if possible. Early in this study, we found that (I) formed rapidly when butyl borate (V) and diisopropoxybis-(diethanolaminoethoxy)titanium(IV) (II) were mixed at room temperature.



In (II) R' = isopropyl, and in (V) R = butyl. (Compound (VI) was similar to (V), with R = —C₆H₄CH₃.)

A latent epoxy resin–catalyst system based on reaction (1), in which (II) and a borate ester are mixed with the epoxy resin, has the following additional advantages:

(1) The borate esters (V) and (VI) and chelated titanium compounds such as (II) are often liquids or low melting solids. Thus, they are easily mixed with the epoxy resins and may even reduce the viscosity of the resin.

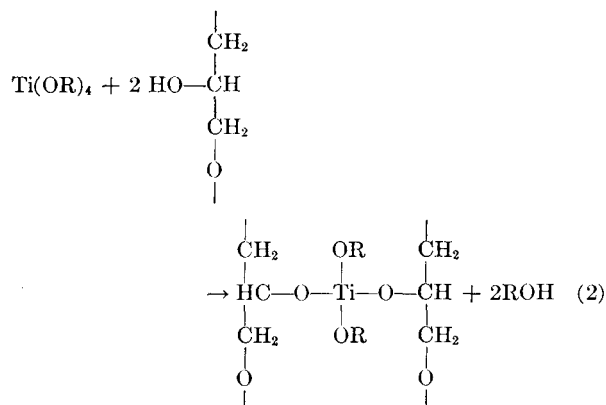
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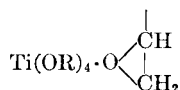
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(2) Triethanolamine (a poor epoxy resin catalyst at best) does not exist in free form in the resin for any long period of time. It is either chelated as in (II) or (Ia), so that its tendency to advance the resin cure at room temperature is minimized.

(3) Titanium esters such as (IV) may also serve as crosslinking agents by transesterification with the resin, as follows:

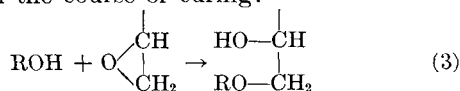


Additional linking by coordination with adjacent ether oxygens is suggested by other work involving tetraalkyl titanates and hydroxyl-containing substances.^{7,8} In addition, molecular complexes such as



could be involved in cleavage of the epoxy rings despite the low electron density in the ethylene oxide ring.⁹ Similar complexes of TiCl_4 and other cyclic ethers have been characterized.¹⁰

(4) The titanium esters and (I) might be expected also to catalyze the addition to epoxide rings of hydroxyl compounds¹¹ produced in reaction (1), so that little volatile material would be produced in the course of curing:



This type of reaction would be particularly likely to occur if ROH were phenolic.¹¹ It would also, of course, act as a chain terminator and decrease crosslinking.

RESULTS AND DISCUSSION

Experiments with epoxy resin B (Table I), in which 5.9 parts each of (II) and butyl borate (approximate molar ratio 1:2) were mixed with 100 parts of resin, showed the proposed catalyst com-

TABLE I
Epoxy Resins

Resin	Epoxy level, eq./100 g.	Esterification level, eq./100 g.	Viscosity (Gardner)
A	0.44-0.48	1.00-1.05	Z-5
B	0.52	1.26	Z-3

bination to be an effective curing agent. These ratios were equivalent to an epoxy resin solution containing about 4 parts triethanolamine borate per 100 parts resin. The titanium-borate ester combination reduced the viscosity of the epoxy resin from Gardner Z-3 to W and gave a gel time of about 50 min. at 150°C. Neither of the components gave gel times approaching this when used with the epoxy resin separately. The resin-curing agent mixture did not attain a viscosity of Z-3 until after standing for two months at room temperature.

The catalyst combination of (II) and butyl borate was found to be a useful one for general coating and adhesive application. However, for casting applications it was necessary to apply vacuum at temperatures of about 80-90°C. before proceeding to cure at elevated temperatures. This prevented bubbling and presumably removed volatile material such as isopropyl alcohol evolved in reaction (1). It was not unexpected that this treatment would be necessary, since in the presence of a secondary alcohol the addition reaction (3) would probably be much slower than with a primary alcohol.¹¹⁻¹³

Since phenols react with the ethylene oxide ring more readily than alcohols,^{11,14,15} a triethanolamine-chelated dicresoxy titanium compound (III) similar to (II) was prepared. This compound has cresoxy ($-\text{C}_6\text{H}_4\text{CH}_3\text{O}$) rather than isopropoxy groups attached to titanium, and can be used with triethyl borate (VI) so that the hydroxyl product of reaction (1) is cresol. This catalyst system was used with a titanium chelate/borate ester molar ratio of 1:2. The catalyst mixture could be premixed, since triethanolamine borate did not tend to precipitate out, or the catalyst components could be added to the resin separately. Gel times of mixtures of Resin A and catalyst at various temperatures and different catalyst concentrations are indicated in Figure 1. A concentration of 10 parts of catalyst per 100 parts resin (phr) is equivalent to about 2.6 phr triethanolamine borate. From Figure 1, it is readily seen that from the viewpoint of gel time, the optimum concentration

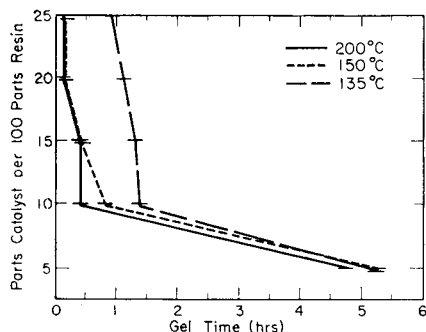


Fig. 1. Effect of concentration of tricresyl borate-cresoxy titanium compound (III) catalyst on gel time of epoxy resin A.

of the titanium compound (III) tricresyl borate catalyst mixture is in the range of 10 to 20 phr.

Where it is desirable, the catalyst system employing titanium compound (II) or (III) may be accelerated by the addition of boron trifluoride-piperidine complex or piperidine. Thus, the gel time at 150°C. of epoxy resin A with 11.8 phr titanium compound(II)-butyl borate catalyst was

TABLE II
Time Behavior of Viscosity of Catalyzed Resin

Recipe	Designation	Viscosity (Gardner)		
		2 weeks	1 month	2 months
Epoxy resin A + 5.9 phr butyl borate + 5.9 phr titanium cpd. (II)	Y	—	—	Z-5-Z-6
As above plus 1 phr piperidine	Y	Gel	—	—
Epoxy resin A + 10 phr titanium cpd. (III)-tricresyl borate	Z-3	—	Z-6	Very viscous
Epoxy resin B + 10 phr titanium cpd. (III)-tricresyl borate	Z-3	—	Z-5	Z-5-Z-6

changed from 50 min. to 15 min. by addition of 1 phr piperidine. The latter, however, seriously diminishes tank life. The tank life of various resin-titanium compound-borate combinations is indicated in Table II, by changes in viscosity over a period of two months. The tank life with the new catalyst system is of the order of two months, longer than for most precatalyzed systems but not as long as for the triethanolamine/borate system.^{3,4}

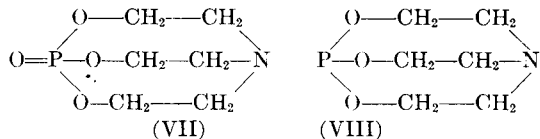
Electrical and Mechanical Properties

Electrical properties of triethanolamine titanate-borate catalyzed epoxy resin mixtures are generally good at elevated temperatures and seem quite suitable for casting applications. Representative data are given in Table III and indicate that good dielectric and loss properties are maintained at 100°C. and do not begin to rise until near 150°C. Generally, when the power factor rises it does so sharply. However, electrical properties are often improved with the additional heating which would take place in equipment operated at elevated temperatures. Surprisingly, additions of small amounts of boron trifluoride-piperidine complex do not seriously impair electrical properties up to 100°C.

Representative mechanical properties for epoxy resins cured with triethanolamine titanate-borate ester curing combinations are given in Table IV. The data compare with those reported elsewhere.¹⁶ The clear improvement in the properties of resin B obtained in going from 10% to 15% catalyst concentration indicates the importance of this factor. The low heat-distortion temperatures are characteristic of resins containing polyether linkages¹⁷ and cured by a tertiary amine mechanism.^{11,18} These temperatures could probably be raised somewhat by using alloying resins and/or glycidyl ether resins of greater functionality¹⁴ than the commercial ones used in this study.

Fire-Resistant Compositions

Other catalyst mixtures imparting different properties to the cured epoxy resin can be formulated by extending the reasoning described thus far. Thus, phosphates or phosphites which may be represented by (VII) or (VIII) or as a low molecular weight polymer with one or two moles of triethanolamine to phosphate or phosphite are readily available or easily prepared. Compounds such as (VII) react readily with borate esters to give (I).



When borate esters were combined with (VII) and (VIII) in the proper molar ratios in epoxy resin formulations, they imparted good fire-resistance properties to cured resin samples, comparable to those imparted by the chlorinated hardener HET

TABLE III
Electrical Properties of Cured Epoxy Resins^a

	Temp., °C.	100 × tan δ		Dielectric constant	
		60 cycles/sec.	1 Kcycles/sec.	60 cycles/sec.	1 Kcycles/sec.
Epoxy resin A + 5.9 phr butyl borate + 5.9 phr titanium cpd. (II)	25	0.35	0.35	3.44	3.43
	100	3.56	2.90	4.19	3.91
	150	8.13	1.17	4.53	4.41
Epoxy resin A + 10 phr tricresyl borate-titanium cpd. (III)	25	0.26	0.42	3.24	3.24
	100	3.67	2.34	3.80	3.61
	150	—	6.95	4.89	4.42
Epoxy resin B + 10 phr tricresyl borate-titanium cpd. (III)	25	0.24	0.26	3.50	3.48
	100	2.01	2.50	5.05	4.89
	150	38.8	3.64	5.35	4.61
	25	0.22	0.29	3.56	3.46
	100	2.77	3.38	4.63	4.38
	150	1.51	—	4.59	4.89
Epoxy resin B + 15 phr tricresyl borate-titanium cpd. (III) + 1% boron trifluoride-piperidine	25	0.25	0.37	3.33	3.31
	100	0.97	0.66	3.56	3.48
	150	17.17	4.14	4.72	4.39

^a All were cured for 24 hr. at 135°C. prior to testing.

TABLE IV
Physical Properties of Epoxy Castings

Recipe ^a	Heat-distortion temp., °C.	Tensile strength, psi	Flexural strength, psi	Flexural modulus, psi	Izod impact, ft. lb./in.	Compressive strength, psi
Epoxy resin A + 10 phr tricresyl borate-titanium cpd. (III)	82	11,260	18,845	473,000	1.00	48,930
Epoxy resin B + 10 phr tricresyl borate-titanium cpd. (III)	70	7,335	15,410	540,000	0.55	18,610
Epoxy resin B + 15 phr tricresyl borate-titanium cpd. (III)	80	7,330	18,465	499,000	0.81	49,275

^a The recipes were cured at 135°C. for 48 hr. prior to testing.

anhydride (hexachloroendomethylene tetrahydrophthalic anhydride), as shown in Table V. In addition, these catalyst systems imparted excellent electrical properties at elevated temperatures (up

to 150°C.) gave good tank life (one month or more), and were easily prepared.

The catalyst compositions described in this paper are given actually only to illustrate an approach. They have proved useful in many applications including casting and encapsulation. By varying the type of borate ester and chelated titanium or phosphorus compound, a wide range of useful catalyst compositions have been formulated which impart a variety of properties to the cured epoxy resin. It is possible also to incorporate many other elements (in addition to phosphorus and titanium) into the resin as desired with the same or similar systems. In view of the numerous possibilities for reaction with the epoxide ring,^{19,20} there is good reason to believe that many curing combinations in addition to amines and anhydrides, which will alter and allow control of the properties of epoxy resins over extended ranges, can be found.

TABLE V
Flammability of Epoxy Resin^a

Material	Burning rate, in./min.	Flame-out time, sec.
Epoxy resin A + 8.45 phr tricresyl borate + 4.8 phr triethanolamine phosphate	0.47	40
Epoxy resin A + 16.9 phr tricresyl borate + 9.65 phr triethanolamine phosphate	0.40	26
Epoxy resin A + 81 phr HET anhydride	0.31	20

^a Tested in accordance with ASTM D365-44. All systems were found to be self-extinguishing.

EXPERIMENTAL

Materials

Borate esters were obtained from U. S. Borax Company and titanate esters from the Pigments Department of E. I. du Pont de Nemours & Co. In some cases it was necessary to remove solvent from the titanate esters. The triethanolamine phosphate was a product of A. R. Maas Chemical Company, South Gate, California. The triethanolamine-chelated titanium cresoxy compound (III) can be prepared in a number of ways. For instance, it was prepared from tetraisopropyl titanate by adding the requisite molar amounts of *m,p*-cresol and triethanolamine and distilling off isopropyl alcohol in a nitrogen atmosphere. At a final flask temperature of 190°C., distillation was discontinued after removal of the calculated amount of isopropyl alcohol.

The mixing of liquid epoxy resins with the liquid titanium compounds and aliphatic borate esters was straightforward, each component being added with stirring until a homogeneous solution was obtained. For more viscous or solid epoxy resins and solid borate esters, the ester or resin (or both) was heated to about 60–70°C. and mixed with stirring until the mixture was homogeneous. The titanium ester was not added until the mixture had cooled to below 60°C.

Electrical properties were measured on cast plates $\frac{1}{8}$ in. thick. Mechanical properties were measured according to standard ASTM procedures.

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Synopsis

New types of catalyst combinations for epoxy resins are described and examples given. These combinations consist of a triethanolamine-chelated titanium compound or phosphorus compound and a borate ester which react to give triethanolamine borate and other epoxy-reactive products. The advantages of these addends as catalysts are ease of mixing with the resin, relatively long tank life (1 to 2 months), good electrical properties at elevated temperatures, and low viscosity where desired. Phosphorus compounds impart fire resistance. It is suggested that the composition of curing combinations of the type described may be varied over a wide range according to the properties desired for the resin-catalyst mixture and the final hardened resin.

Résumé

On décrit des nouveaux types de combinaisons catalytiques pour les résines époxyées et on en donne des exemples. Ces combinaisons consistent en un composé chélaté titane-triéthanolamine, ou en un composé phosphoré et un ester borique qui réagit pour donner un borate de triéthanolamine et d'autres produits réagissant avec la fonction époxyée. Les avantages de ces produits ajoutés comme catalyseurs sont: la facilité de mélange avec la résine, la durée relativement longue de conservation (1 à 2 mois), de bonnes propriétés électriques à températures élevées, et une faible densité quand on le désire. La résistance thermique est une caractéristique du composé phosphoré. On propose que des combinaisons vulcanisantes du type décrit, soient transformées sur une large gamme de compositions, en accord avec les propriétés désirées du mélange catalytique et en accord avec le durcissement final de la résine.

Zusammenfassung

Neue Typen von Katalysatorkombinationen für Epoxyharze werden beschrieben und Beispiele angeführt. Diese Kombinationen bestehen aus einer mit Triäthanolamin chelierten Titan- oder Phosphorverbindung und einem Boratester, dessen Reaktion Triäthanolaminborat und andere epoxyreaktive Produkte ergibt. Die Vorteile dieser Zusätze als Katalysatoren sind leichte Mischbarkeit mit dem Harz, relativ lange Lagerfähigkeit (1–2 Monate), gute elektrische Eigenschaften bei erhöhten Temperaturen und, falls erwünscht, geringe Viskosität. Bei Verwendung von Phosphorverbindungen wird auch Feuerbeständigkeit erreicht. Es wird darauf hingewiesen, dass Behandlungskombinationen der beschriebenen Art entsprechend den gewünschten Eigenschaften der Harz-Katalysatormischung und des gehärteten Harzes als Endprodukt über einen grossen Zusammensetzungsbereich variiert werden können.

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