Metal Acetylacetonates as Latent Accelerators for Anhydride-Cured Epoxy Resins

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

Synopsis

Twenty-two metal acetylacetonate compounds have been evaluated as possible latent accelerators for epoxy-anhydride solventless resins. Experimental data have revealed that titanium (IV) oxyacetylacetonate, chromium (III), zirconium (IV), cobalt (III), and cobalt (II) acetylacetonates are particularly effective with anhydride cured epoxy resins. When added to the resin at a level of 0.05–0.10% (w/w), they provide very fast gel times at 150–175°C combined with very good storage stabilities (> six months) at room temperature. The power factor values of cured resin samples, containing these preferred metal acetylacetonates, have been found to be between 2.0 and 2.5% at 150°C and 60 Hz. Correlation between the catalytic effectiveness of these metal acetylacetonates, as latent accelerators for epoxy-anhydride resins, and their thermal stabilities suggest that decomposition products may be the active species responsible for initiating polymerization in epoxy-anhydride resin systems.

INTRODUCTION

A considerable amount of effort has been devoted in recent years, mainly in the industrial laboratories, to develop a "perfect latent" catalyst for curing epoxy resins.

The properties desired of such a material are the following:

(1) It should give rapid cure of epoxy resins at moderately elevated temperatures (e.g., <60 min at 135–180°C).

(2) It should be completely miscible with the resins at all temperatures. This is particularly true of impregnating resins.

(3) The storage life of the catalyzed resin should be indefinite. In practice, the viscosity of the resin should not change appreciably at room temperature after periods of several months to years.

(4) It should not adversely affect the properties of the cured resin. In particular, the electrical and mechanical properties of the resin should not be affected by the catalyst.

Numerous patents[1–3] have been issued in recent years on the development of latent catalysts for DGEBA (i.e., bisphenol A-type) resins, but most fulfill only a few of the conditions outlined. One of the most successful of these has been the boron trifluoride–monoethylamine complex[4] (BF_3·MEA or BF_3·400), which is presently used commercially for curing DGEBA epoxy resins. However, one of the serious disadvantages of this particular latent catalyst is its poor electrical properties at elevated temperatures.

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 the epoxy technological field to use anhydride

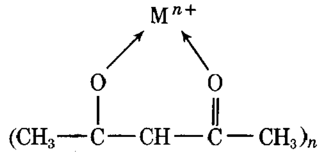
Journal of Applied Polymer Science, Vol. 26, 979–986 (1981)

CCC 0021-8995/81/030979-08$01.00

curing agents with DGEBA epoxy resins.[5] Most anhydride formulations require elevated-temperature cures with the ultimate properties depending on postcures at temperatures of 150°C or higher.

For most commercial applications utilizing anhydride-cured epoxy resins, it is necessary to add some form of accelerator to the formulation to speed the rate of cure. In the last few years, quaternary phosphonium[6,7] and arsonium[8,9] compounds have been disclosed as latent accelerators for anhydride-epoxy impregnants. These materials, however, are not true organometallic compounds (i.e., the inorganic atom is not a real "heavy metal").

Recently, we have discovered that certain organometallic compounds, based on transition metal elements and acetylacetonates, are extremely effective latent accelerators for the carboxylic anhydride cure of bisphenol A epoxy resins. These organometallic compounds have the generalized composition



$$\begin{array}{c} M^{n+} \\ \nearrow \qquad \nwarrow \\ (CH_3-\overset{\overset{O}{|}}{C}-CH-\overset{\overset{O}{\|}}{C}-CH_3)_n \end{array}$$

where M is a metal atom and n^+ is the ionic charge on the atom.

Metal acetylacetonate compounds have been described previously in the scientific literature[10–13] as catalytic curing agents for epoxy resins. Starck and Schlenker[10] employed them as catalysts to cure phenolaldehyde condensates (both filled and unfilled resins) with glycidyl polyethers. Naps[11] cured polyepoxy resins by using multivalent metal salts of acetoacetic acid ester, malonic acid ester, acetylacetone, formylacetophenone, and formylacetone. The metal chelate salts of Cu^{2+} were of particular interest in this application. Phenolic accelerators have been described by Markovitz[12] for curing epoxy resins using titanium and zirconium acetylacetonates as catalysts.

None of these cited references indicate that metal acetylacetonates can be used as latent *accelerators* for carboxylic anhydride cure of bisphenol A epoxides. Although epoxy molding compositions, cured with anhydrides, have been described,[14] there has been no suggestion that low viscosity (i.e., <500 cP) solventless epoxy resins, with long storage lifetimes, could be formulated using certain *selected* metal acetylacetonates in conjunction with a liquid carboxylic anhydride.

As the results will show, some metal acetylacetonates are suitable for this application, whereas many others are not.

EXPERIMENTAL AND RESULTS

Metal Acetylacetonates Evaluated

The 22 metal acetylacetonates investigated are shown in Table I. Most of the evaluation studies were made using a 1:1 stoichiometric bisphenol A epoxy–anhydride formulation. The anhydride component used was a liquid anhydride, 1-methyltetrahydrophthalic anhydride (Union Carbide commercial designation ZZLA-0334). The metal acetylacetonates were added to the combined epoxy–anhydride resin at a level of 0.05–0.10% (w/w). As the data will show, however,

TABLE I
Various Metal Acetylacetonates Evaluated as Latent Accelerators for Epoxy–Anhydride Resins

Metal acetylacetonate	Formula
Titanium oxyacetylacetonate	$TiO(C_5H_7O_2)_2$
Aluminum acetylacetonate	$Al(C_5H_7O_2)_3$
Cerous acetylacetonate	$Ce(C_5H_7O_2)_3$
Manganese (II) acetylacetonate	$Mn(C_5H_7O_2)_2$
Iron (III) acetylacetonate	$Fe(C_5H_7O_2)_3$
Magnesium acetylacetonate	$Mg(C_5H_7O_2)_2$
Manganese (III) acetylacetonate	$Mn(C_5H_7O_2)_3$
Cobalt (II) acetylacetonate	$Co(C_5H_7O_2)_2$
Copper (II) acetylacetonate	$Cu(C_5H_7O_2)_2$
Chromium (III) acetylacetonate	$Cr(C_5H_7O_2)_3$
Nickel acetylacetonate	$Ni(C_5H_7O_2)_2$
Zinc acetylacetonate	$Zn(C_5H_7O_2)_2$
Cobalt (III) acetylacetonate	$Co(C_5H_7O_2)_3$
Vanadium (III) acetylacetonate	$V(C_5H_7O_2)_3$
Uranyl acetylacetonate	$UO_2(C_5H_7O_2)_2$
Zirconium acetylacetonate	$Zr(C_5H_7O_2)_4$
Thorium acetylacetonate	$Th(C_5H_7O_2)_4$
Strontium acetylacetonate	$Sr(C_5H_7O_2)_2$
Sodium acetylacetonate	$C_5H_7O_2Na$
Potassium acetylacetonate	$C_5H_7O_2K$
Lead acetylacetonate	$Pb(C_5H_7O_2)_2$
Beryllium acetylacetonate	$Be(C_5H_7O_2)_2$

some insolubility with some of the metal acetylacetonates was found even on heating the resin up to 100°C.

Gel Time Data

Gel times were recorded at 135, 150, and 175°C, with 10- to 20-g samples of resin in an aluminum dish placed in a forced-air oven. Typical data found are shown in Figure 1 and in Table II for the 22 metal acetylacetonate compounds evaluated. In most instances, the aluminum dish was covered with a clock glass during the initial gel stage.

Storage Data

The storage properties of the various samples at room temperature were evaluated using a Gardner–Holdt bubble tube viscometer (ASTM D154-56). The shelf life was measured as the time taken for the resin samples to attain 1000 cps at room temperature. Typical viscosity cures for eight of the metal acetylacetonates in the epoxy anhydride resin, over a 90-day storage period, are shown in Figure 2.

Electrical Properties

Electrical properties were obtained on 2-in. diam disks ($\frac{1}{8}$–$\frac{1}{4}$ in. thick) of cured resin. The power factor ($100 \times \tan \delta$) and dielectric constant (ϵ') data, obtained at 150°C and 60 Hz, for the various metal acetylacetonates, are summarized in Table III. The effect of temperature on dissipation factor for a resin sample,

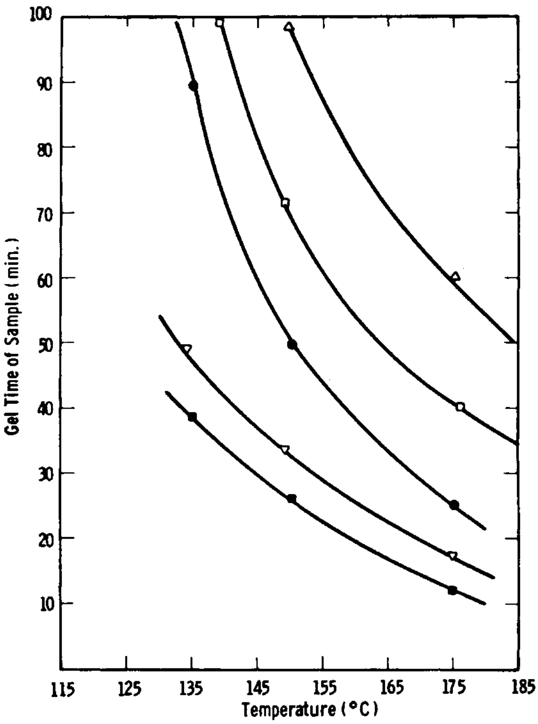


Fig. 1. Gel time data for epoxy-anhydride resin containing various metal acetylacetonates [~0.10% (w/w) on resin]: △, beryllium acetylacetonate; □, vanadium acetylacetonate; ●, chromium acetylacetonate; ■, potassium acetylacetonate; ▽, sodium acetylacetonate.

containing 0.10% w/w of chromium acetylacetonate, is shown in Figure 3. The test samples used in these studies were all cured overnight at 150°C (i.e., 16 hr).

DISCUSSION

Examination of the experimental results in Tables II and III for the epoxy-anhydride resin reveals that the metal acetylacetonates, which give the best combination of latency, fast gel times, and low power factor values, are those of titanium (IV), chromium (III), cobalt (III), zirconium (IV), aluminum (III), manganese (III), and cobalt (II). None of the other compounds evaluated showed this satisfactory compromise of properties. Iron (III) acetylacetonate, however, may be worthy of further evaluation since, at lower concentrations than 0.10% in the epoxy-anhydride impregnant, a more suitable compromise between storage life time and gel time may be attainable.

At this time, it is not very clear why the acetylacetonates of titanium (IV), chromium (III), manganese (III), cobalt (II), and cobalt (III), zirconium (IV), and aluminum (III) should be such powerful latent accelerators for epoxy-anhydride resins and be so much more effective than the other metal acetylacetonates investigated. The only apparent "common link" between some of these materials is that they are all *transition metal* acetylacetonates and are (along with iron) adjacent to each other in the Periodic Table [e.g., Cr (III), Mn (III),

TABLE II
Gel Time and Storage Data for Epoxy–Anhydride Resin with Different Metal Acetylacetonate Accelerators

Sample No.	Metal acetylacetonate used (0.10% on impregnant)	Gel time data (min)[a]		Catalyzed storage lifetime at 25°C, days[b]
		150°C	175°C	
1	Titanium oxyacetylacetonate	35–40	30–35	110
2	Aluminum acetylacetonate	35–40	30–35	95
3	Cerous acetylacetonate[c]	—	50–55	—
4	Manganese (II) acetylacetonate[c]	—	55–65	—
5	Iron (III) acetylacetonate	—	<15	<10
6	Magnesium acetylacetonate[c]	—	50–55	—
7	Manganese (III) acetylacetonate	80–90	40–45	160
8	Cobalt (II) acetylacetonate	50–55	35–40	130
9	Copper (II) acetylacetonate[c]	—	90–100	—
10	Chromium (III) acetylacetonate	40–50	30–40	>200
11	Nickel acetylacetonate	—	45–50	>90
12	Zinc acetylacetonate[c]	—	20–25	50
13	Cobalt (III) acetylacetonate	80–90	25–35	>200
14	Vanadium (III) acetylacetonate	70–80	40–45	>90
15	Uranyl acetylacetonate	<10	<10	<4
16	Zirconium acetylacetonate	50–55	30–35	>90
17	Thorium acetylacetonate[c]	60–65	50–55	—
18	Strontium acetylacetonate[c]	100–110	60–65	—
19	Sodium acetylacetonate	35–40	20–25	>90
20	Potassium acetylacetonate	25–30	15–20	>90
21	Lead acetylacetonate[c]	100–110	70–80	—
22	Beryllium acetylacetonate	100–110	60–65	>90

[a] On 10-g impregnant sample in 2-in. diam aluminum dish.
[b] Time for viscosity to reach 1000 cps at 25°C (some values obtained by extrapolation of data).
[c] Poor or partial (<50%) solubility in resin.

Co (II), and Co (III)]. However, this interpretation makes it difficult to explain why manganese (II) is, apparently, less effective than manganese (III).

Although the insolubility of some of the acetylacetonates may have been a contributing factor in explaining their widely differing catalytic behaviors with epoxy-anhydride resins, the actual mechanism responsible for their effectiveness may be related to the tendency of some of these materials to decompose or dissociate at elevated temperatures. The technique of organic particulate analysis (OPA) has been employed by us in evaluating the thermal decomposition of the same 22 metal acetylacetonates evaluated in the present work.[15,16] Very strong particulation below 190°C was observed with about half of these compounds, particularly with the transition metal acetylacetonates, such as Co (II), Co (III), Fe (III), Cr (III), Mn (III), Zn (II), Al (III), and Cu (II), indicating substantial decomposition of these compounds at temperatures between 95 and 170°C.

Since the most effective latent accelerators would appear to be the ones which undergo thermal decomposition in the 95–170°C temperature range, the decomposition products may, in fact, be the active species responsible for the initiation of polymerization in epoxy-anydride resins. The actual catalytic species involved may be metal cation, metal oxide, or other ionic fragments, and the initiation mechanism probably involves interaction of this species with the carboxylic anhydride component, resulting in opening of the ring structure.

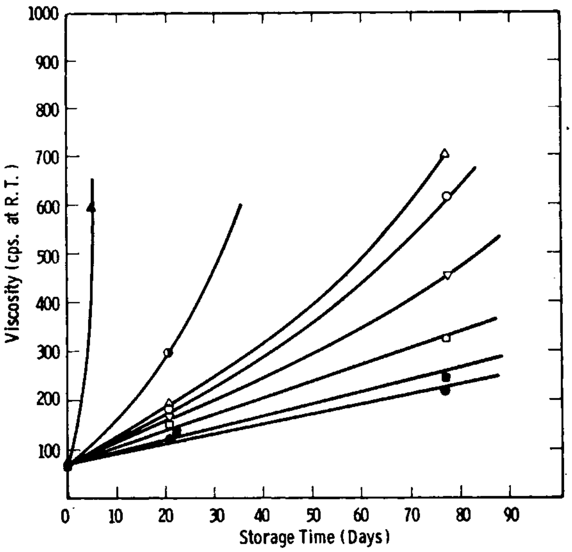


Fig. 2. Viscosity storage data for epoxy–anhydride resin with various metal acetylacetonates [0.10% (w/w) on resin]: ▲, iron (III) acetylacetonate, zinc acetylacetonate; △, aluminum acetylacetonate; ○, titanium acetylacetonate, ▽, cobalt (II) acetylacetonate, □, manganese (III) acetylacetonate, ■, cobalt (III) acetylacetonate, ●, chromium (III) acetylacetonate.

Metal cation formation would appear to be the most likely thermal degradation product route for many of these metal acetylacetonates. Although complex formation between epoxy moiety and metal cations are possible in these resin

TABLE III
Electrical Properties for Cured Samples of Epoxy–Anhydride Resin with Different Metal Acetylacetonate Accelerators

Sample No.	Metal acetylacetonate used (~0.10% on resin)	Electrical properties at 150°C and 60 Hz[a]	
		100 × tan δ	ε′
1	Titanium oxyacetylacetonate	2.4	6.7
2	Aluminum acetylacetonate	2.5	6.9
3	Cerous acetylacetonate[b]	8.0	6.9
4	Manganese (II) acetylacetonate[b]	43.0	6.8
5	Iron (III) acetylacetonate	1.6	6.4
6	Magnesium acetylacetonate[b]	1.8	7.1
7	Manganese (III) acetylacetonate	5.3	7.4
8	Cobalt (II) acetylacetonate	2.8	6.6
9	Copper (II) acetylacetonate	310.0	19.0
10	Chromium (III) acetylacetonate	2.0	7.4
11	Nickel acetylacetonate	2.2	6.7
12	Zinc acetylacetonate[b]	112.0	9.8
13	Cobalt (III) acetylacetonate	2.2	6.9
14	Vanadium (III) acetylacetonate	1.8	6.5
15	Uranyl acetylacetonate	15.0	7.9
16	Zirconium acetylacetonate	4.7	7.6
19	Sodium acetylacetonate	12.0	7.9
20	Potassium acetylacetonate	27.0	8.4

[a] Samples cured 16 hr at 150°C (~0.200 in. thick).

[b] Metal acetylacetonate concentrations in impregnants probably <0.05%.

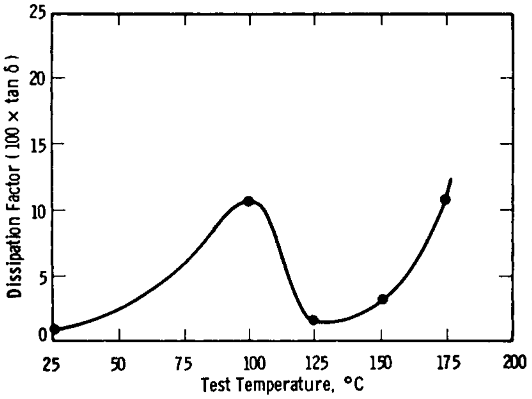
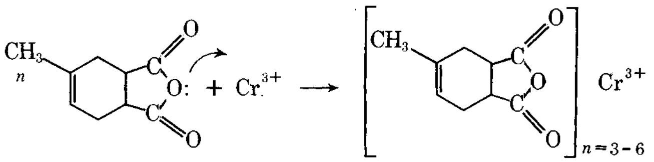


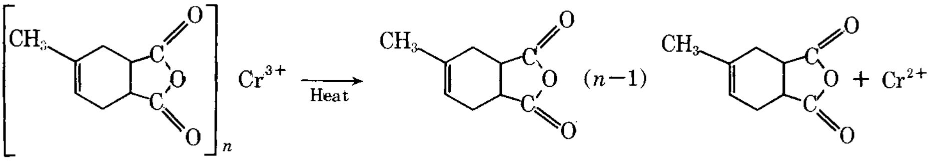
Fig. 3. Variation of dissipation factor (100 × tan δ) with temperature for epoxy–anhydride resin containing 0.10% (w/w) of chromium acetylacetonate.

systems, the more likely initiation mechanism would appear to be one involving electron transfer between carboxylic anhydride and the liberated metallic cations to give a reactive initiating species.

For example, with 1-methyltetrahydrophthalic anhydride (ZZLA-0334), the following electron transfer step could occur with a metallic cation, such as chromium (III), to give a transient complex species:



Dissociation of this complex at elevated temperature will lead to the formation of epoxy-reactive anhydride species and the reduction of chromic (III) cation to chromous (II):



The reactive anhydride species is probably one where an oxonium-type cation is formed by donation of an electron from the central oxygen on the anhydride ring to the chromium III (chromic) cation (thereby reducing chromium III to chromium II). The carboxylic cationic species will then be free to initiate rapid polymerization of the resin components. This rapid cationic polymerization will probably occur with both anhydride and epoxy molecules resulting in rapid gel formation. Evidence for this initiation mechanism with chromium cations is given by the fact that during cure of the epoxy-anhydride resin, in the presence of chromium (III) acetylacetonate, the characteristics *brown–red* coloration of chromium III (chromic) ion changes to *green* after cure, indicating reduction to chromium II (chromous) ion.

The initiation mechanism described previously is only one of several possibilities. Other thermal degradation reactive species would probably interact with the epoxy-anhydride components in a different manner than metal cations. In addition, the metal acetylacetonates which exhibit catalytic behavior *without* thermal decomposition must obviously accelerate resin cure in a totally different manner than the heat-sensitive compounds.

Regarding the effects of some of these metal acetylacetonates on the electrical properties of the cured epoxy-anhydride resin, the extremely high power factor values shown by the resin samples containing manganese (II), zinc, and copper acetylacetonates (Table III) are interesting and deserve further investigation. Although insufficient cure of resin might be responsible for the high values found with the copper and manganese (II) compounds (both these compounds display sluggish gel times at 175°C), this explanation would not hold for the zinc acetylacetonate which exhibits a fast gel time at 175°C. Possibly metal-catalyzed oxidation degradation reactions in the epoxy resin during postcure might be responsible.

References

1. I. N. Elbling and A. B. Finestone, Ger. Pat. 1,162,439 (Nov. 1958).
2. L. F. Betnamont, Br. Pat. 869,969 (1961).
3. W. R. Proops and G. W. Fowler, Br. Pat. 966,917 (1965).
4. A. J. Landua, *Am. Chem. Soc. Div. Org. Coatings Plast. Chem. Prepr.*, **24** (2), 299 (1964).
5. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 5, p. 20.
6. J. D. B. Smith, U.S. Pat. 3,784,583 (1974).
7. J. D. B. Smith, *J. Appl. Poly. Sci.*, **23**, 1385 (1979).
8. J. D. B. Smith, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.* **39** (1978).
9. U.S, Pat. 3,979,355 (1976).
10. H. Starck and F. Schlenker, U.S. Pat. 2,801,228 (1957).
11. M. Naps, U.S. Pat. 2,876,208 (1959).
12. M. Markovitz, U.S. Pat. 3,812,214 (1973).
13. K. Kaeriyama, *Makromol. Chemie*, **175**, (8), 2285 (1974).
14. J. J. Miyashiro and A. W. Selling, U.S. Pat. 3,624,032, (1971).
15. J. D. B. Smith, D. C. Phillips, and T. D. Kaczmarek, *Microchem. J.*, **21**, 424 (1976).
16. D. C. Phillips and J. D. B. Smith, *Anal. Lett.*, **9** (8), 744 (1976).

Received June 24, 1980
Accepted August 27, 1980