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Development of Chlorendic Anhydride-Cured Epoxy Systems with Wide Variations in the Resin : Anhydride Ratio

M. F. LEVY and M. J. CANESTARO, *CPM Process Engineering and MRL, IBM Corporation, Endicott, New York 13760*

Synopsis

Using the epoxy resins Epon 828 (diglycidyl ether of bisphenol A) and DEN 438 (an epoxylated novalak) with chlorendic anhydride as the curing agent, a series of formulations were developed having a very wide range in the anhydride: resin ratio (40–160 phr). This range was made possible by the use of metal chelate catalysis. While these systems were not evaluated for fire retardancy, it is anticipated that they would exhibit this property dependent on their chlorine contents.

INTRODUCTION

This work was initiated as part of a study of anhydride curing agents as a class, coupled with an interest in the catalytic effect of metal chelates on epoxy systems. While no exhaustive survey of anhydride curing agents or chelates was made, we observed that epoxy systems cured by Nadic Methyl or hexahydrophthalic anhydrides were unaffected by VOA_2, FeA_2, and CoA_2 (where A is acetylacetonate). Chlorendic anhydride systems, on the other hand, behaved quite differently. The relative extents of ester and ether bond formation, and consequently the optimum resin: anhydride ratio, varied with the chelate used as catalyst, as evidenced by the variation in optimum chlorendic anhydride required.

Further evidence of this variation was seen in the infrared spectra of DEN 438 formulations catalyzed by VOA_2 and by CoA_2. Using the 1750 and 1195 ester, 1115-cm^{-1} ether peak absorbance ratios (ester: ether) of 1.33 and 1.51 were obtained with VOA_2; these values were 0.92 and 1.01 with the CoA_2-catalyzed sample.

Table I shows how a number of acetylacetonates affected the stroke cure of an Epon 828–chlorendic anhydride (132.4 phr)–acetone varnish during 24-hr storage at ambient temperature.[1] The quantities of chelate were selected so that each sample would have about the same atomicity of metal.

The zinc and aluminum chelates were too fast and too slow, respectively, and were not investigated further. Systems containing those chelates providing the five most time-stable varnishes were optimized in solvent-free

TABLE I

Chelate	phr	Stroke cures, sec		
		Immediate	After 24 hr	Change
ZnA_2	3.2	59	—	—
CuA_2	3.2	400	625	225
NiA_2	3.1	220	173	47
CoA_3	4.4	125	114	9
CoA_2	3.1	120	107	13
FeA_3	4.4	150	115	35
FeA_2	3.1	184	172	12
MnA_3	3.4	130	29	51
MnA_2	3.1	178	125	53
CrA_3	4.4	298	165	133
VOA_2	3.2	200	184	16
VA_3	4.3	182	109	73
$TiOA_2$	3.1	255	133	122
ZnA_4	6.0	126	76	50
AlA_3	4.0	396	—	—

systems with respect to chlorendic content and cure time to give the highest distortion temperatures.[2]

EXPERIMENTAL

The chelates were the products of MacKenzie Chemical Works and were used without purification. Epon 828 is a product of Shell Chemical Co.; DEN 438, a product of Dow Chemical Co.; and chlorendic anhydride, a product of Hooker Chemical Corp.

The Epon 828 systems were gelled for 8 hr at 180°C and then cured at 200°C until no further increase in distortion temperature was observed. Similarly, the DEN 438 systems were gelled at 180°C for 3.5 hr and then cured at 200°C.

TABLE II
Epoxy Resin Epon 828-Chlorendic Anhydride Systems

Catalyst	Concn, phr	Chlorendic anhydride, phr	Cl, % (calcd)	DT °C	Cure, hr
none[a]	—	117.2	31.0	204	24[b]
BDMA	0.4	160	35.3	223	22
VOA_2	3.5	132	32.7	210	8
FeA_2	2.1	132	32.7	211	6
CoA_2	2.0	80	25.4	195	13
CoA_3	4.4	90	27.1	189	8[b]
NiA_2	3.0	80	25.4	198.5	8

[a] From Hooker Chemical Corporation, *Bulletin 43*.[3]
[b] Cured at 180°C, only for indicated time.

TABLE III
Epoxy Resin DEN 438—Chlorendic Anhydride Systems

Catalyst	Concn, phr	Chlorendic anhydride, phr	Cl, % (calcd)	DT, °C	Cure, hr
BDMA	0.2	140–160	33.5–35.3	234–235	10
VOA_2	2.0	120–140	31.2–33.5	230	11
FeA_2	2–3	100–120	28.6–31.2	230–235	10
CoA_2	2.0	40–60	16.4–21.4	243	22
CoA_3	4.4	60	21.4	223	4
NiA_2	3.1	80	25.4	240	11

RESULTS

The several systems evaluated are shown in Tables II and III. A standard catalyst, benzyldimethylamine (BDMA), and an Epon 828 self-catalyzed system are included for comparison.

The use of metal chelate catalysts in the chlorendic anhydride cure of Epon 828 and DEN 438 provides a means for attaining maximum distortion temperatures while allowing very wide ranges in anhydride content.

References

1. *SPI Handbook of Reinforced Plastics*, Appendix II-2.5, p. 67 (1964).
2. ASTM D-621-64 (1968).
3. Hooker Chemical Corporation, *Bulletin 43*, p. 12., Hooker Chem. Corp. (1956).

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