Catalysis of the Epoxy-Carboxyl Reaction

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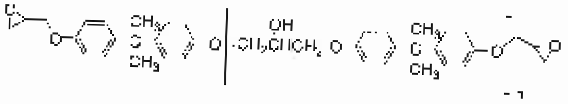
We have investigated the reactions of glycidyl ether, glycidyl ester, and other oxirane functional resins with carboxyl or anhydride functional compounds and polymers in the presence of a wide range of amine, phosphonium, and metal catalysts.

We confirmed that both amine and phosphonium compounds can catalyze the reaction of epoxy groups with carboxyl and anhydride groups. There are certain deficiencies with these catalysts, such as a tendency to yellow and a reduction in stability at ambient or elevated temperatures. We also observed that many of the known amine catalysts contribute to poorer humidity resistance and exterior durability. Several metal salts were found to be effective catalysts, but they also contributed to a reduction in chemical resistance or they led to paint instability.

We have discovered a group of metal chelates that overcome these problems and provide stable formulations in a single package that do not yellow during cure and that give improved resistance properties. The new catalysts have been evaluated in high-solids epoxy/carboxyl coatings, automotive clearcoats, and powder coatings.

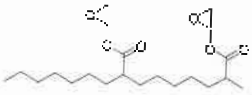
INTRODUCTION

Epoxy resins represent a commercially important segment of the polymer industry. Epoxy resins are used in different applications, such as coatings, adhesives, laminates, castings, encapsulations, and moldings. What distinguishes epoxy resins from other polymers are their excellent chemical resistance properties, excellent adhesion, and versatility in crosslinking. The oxirane, or epoxy ring, can be homopolymerized or reacted with active hydrogen containing compounds, such as amines, phenols, or acid.[1] Nearly all of the epoxy resins used in coating applications are based on bisphenol A diglycidyl ether resins. To a smaller extent glycidyl ethers of aliphatic alcohols are used as reactive diluents. A structure of a typical bisphenol A diglycidyl ether resin is shown below. For liquid resins n is close to zero. For solids resins n can be between 3-30. Liquid bisphenol A diglycidyl ether resins are used mainly in room temperature curing applications, such as high-solids coatings in conjunction with amine curing agents. The higher MW polymeric bisphenol A resins are normally applied in bake applications. For instance, in coatings for cans and in coil primer applications epoxy resins are used as polyols and are crosslinked with amino resins.



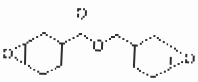
Bisphenol A diglycidyl ether

Glycidyl ester resins, predominately glycidyl methacrylate ester copolymers, are used in powder coatings for exterior durable applications. Glycidyl ether and glycidyl ester resins are usually prepared by reaction of epichlorohydrin with either a phenol or a carboxylic acid respectively.



Glycidyl ester functional acrylic resin, only the glycidyl functional groups are shown. Glycidyl functional acrylic resins produce coatings with excellent exterior durability.

Another type of epoxy resin is the cycloaliphatic resin. An example of these resin are 3,4-epoxycyclohexane-methyl-3,4-epoxycyclohexane carboxylate.[2]



Cycloaliphatic epoxies are prepared by epoxidation of the appropriate unsaturated compound with a peracid.[2]

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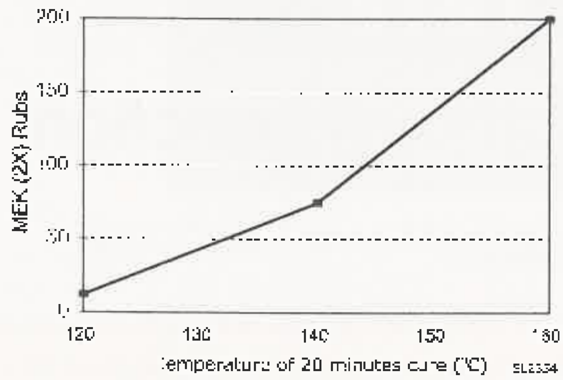
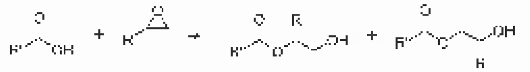


Figure 1—MEK solvent resistance of glycidyl ester and carboxyl functional acrylic resin epoxy/COOH. 1/1. Film thickness 25 micron.

The reaction of epoxy groups with carboxyl and anhydride groups is of great practical and economic importance in the coating and polymer industry. Because this reaction is a ring opening condensation reaction, it does not produce any reactive volatiles as substitution reactions do. The crosslinks formed are stable linkages with excellent chemical resistance properties.

For many industrial coating applications, where excellent resistance properties and low yellowing are required, the reaction of epoxy resins with carboxyl or anhydride groups is used as a crosslinking mechanism. Many powder coating systems use glycidyl ether functional bisphenol A resins in combination with carboxyl terminated polyester[4] resins to achieve outstanding physical and chemical resistance properties. Most acrylic powder coatings utilize glycidyl ester functional acrylic polymers and 1,12-dodecanedioic acid as a crosslinker.[5] Although the reaction of an epoxy group with a carboxyl group can proceed in the absence of a catalyst for many applications, catalysis is required to achieve acceptable reaction rates.

In the uncatalyzed reaction of epoxy groups with carboxyl groups four reaction products are to be expected[6] [equations (1-4)]. In the ring opening reaction of the epoxy group with a carboxyl group, two different reaction products are formed. One is the ester of the primary hydroxyl group, and the second is the ester of the secondary hydroxyl group [equation (1)]. The reaction does not stop here. With glycidyl ether type epoxy groups, the reaction temperatures are high enough that esterification of the reaction product in equation (1) to a complete esterified product also takes place [equation (2)]. An additional reaction one has to contend with is the reaction of the hydroxyl groups obtained in reaction [equation (1)] with epoxy groups leading to ether formation [equation (3)]. The water formed [equation (2)] can also lead to hydrolysis of the epoxy group. The formation of ether groups [equation (3)] will proceed only in the presence of an excess of epoxy groups. In an open system, such as a film, the hydrolysis of epoxy groups [equation (4)] is of minor consequence. Because of the increase in rate of reaction [equation (1)] the reaction [equation (2)] is suppressed under base-catalyzed conditions. The formation of ether linkages is more of a problem in the presence of an acid catalyst.[7] Ether linkage formation can be a concern in exterior durable coatings because of the poorer UV resistance of ether containing polymers.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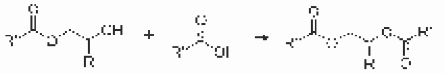
(2)


(3)


(4)

Base catalysis is often used to speed up the reaction between carboxyl groups and epoxy groups. Under base catalyzed conditions, an anionic mechanism is most probable. The rate of reaction is controlled by the type and concentration of catalyst because the rate is determined by the decomposition of the acid salt formed between the carboxyl group and the basic catalyst.[8]

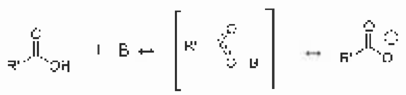
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Table 1—Cure Response of Glycidyl Ester and Carboxyl Functional, 0.005 mol% Catalyst on Resin Solids

Baking Schedule Catalyst	110°C, 15 min MEK Double Rubs	140°C, 15 min MEK Double Rubs	Viscosity 0 hr, cps	Viscosity 7 Weeks, cps
No catalyst (control)	10	40	298	340
2 Ethylhexyl amine	—	34	418	770
Bis(2-ethylhexyl)amine	—	41	400	480
Tetrabutyl phosphonium bromide		40	280	360
Proton sponge	5	62	350	gelled
Dodecyldimethylamine	12	105	360	gelled
N,N-Dimethylbenzylamine	6	142	344	gelled
2 Ethyl Imidazole	16	140	308	gelled
DBU/Octanoic acid	5	179	318	gelled
Tetramethyl guanidine	6	175	405	gelled
Benzyltrimethyl ammonium bromide	34	>200	116	gelled
Benzyltrimethyl ammonium hydroxide	20	>200	320	gelled
Tetrabutyl ammonium hydroxide	19	>200	320	gelled

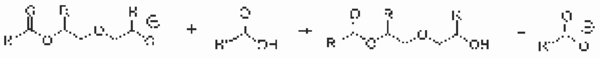
Drawdown on steel panels. 1 mil (25 micron) dry film thickness.

Table 2—Overbake Yellowing and Humidity Resistance of Glycidyl Ester and Carboxyl Functional Acrylic Resin, 0.005 mol% Catalyst on Resin Solids

Catalyst	Yellowing Index b*[30] 180°C, 20 min	Humidity Resistance Cleveland Condensing, Gloss 20°, % 0 Days	21 Days	35 Days
No catalyst	0.20	87.1	87.1	87.1
N, N-Dimethy benzylamine	2.77	89.7	86.6	86.6
2 Ethyl imidazole	2.79	91.0	86.3	81.6
DBU/2-ethyl hexanoic acid	1.64	90.7	91.1	88.4
Tetramethyl guanidine	1.27	86.6	86.5	85.3
Benzyltrimethyl ammonium bromide	2.14	94.1	79.2	75.4
Benzyltrimethy ammonium hydroxide	2.64	91.1	78.0	83.1
Tetrabutyl ammonium hydroxide	1.12	87.1	82.5	75.6

b* Refers to the yellowing Index of the CIELAB Color Model. See also Table 13.


(6)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(8)

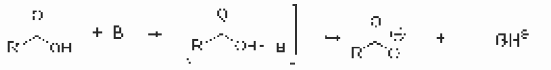
The catalytic activity of different bases[9] was found to decrease in the following order: pyridine[10]>isoquinoline>quinoline>N,N-dimethyl-cyclohexylamine>tributylamine>N-ethyl morpholine >dimethylaniline>potassium hydroxide. This order of reaction would be different if these compounds were used as curing catalysts for coatings, due to the evaporation in thin films. A tertiary amine catalyst can also be incorporated as an internal catalyst into acrylic polymers and this approach is often taken for can coatings.

Quaternary ammonium and phosphonium compounds were found to be excellent room temperature catalysts for automotive refinishing.[11]

In recent work the catalyzed reaction of water dispersed polymers having tertiary amine functionality was studied with glycidyl ester functional emulsions at room temperature.[12] The actual mechanism of crosslinking was not the reaction of the epoxy groups with the carboxyl groups, but rather the formation of quaternary ammonium groups and subsequent salt formation of the quaternary ammonium groups with the carboxyl groups [equation (8)].

Imidazoles have been found to be very effective catalysts for the epoxy-carboxyl reaction.[13] A variety of imidazoles with different substitutions and pKa values are commercially available. Imidazoles were found to show superior catalysis to dicyandiamide in powder coatings.[14]

Another potential mechanism, which has been suggested with amine catalysts, is the activation of the ether linkage as shown in the reaction schemes in equations (9-14).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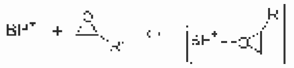
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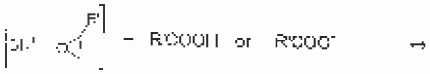
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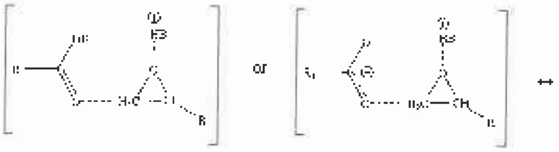
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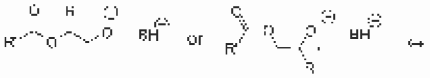
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Table 3—Cure Response of Glycidyl and Carboxyl Functional Acrylic Resin, 0.28% Me Catalyst on Resin Solids

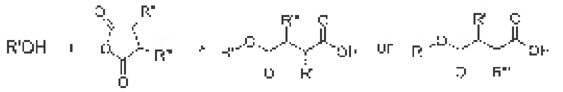
Cure Conditions Catalyst	140°C, 15 min MEK Double Rubs	Viscosity 0 Hours, cps	Viscosity 6 Weeks, cps
No Catalyst	40	278	320
Aluminum acetylacetonate	49	140	70
Aluminum lactate	34	110	155
Bismuth octoate	52	310	408
Calcium octoate	53	285	580
Cerium naphthenate	50	270	540
Chromium(II)2-ethylhexanoate	—	Gelled	—
Cobalt octoate	—	Gelled	–
Copper(I)acetylacetonate	48	120	155
Iron(III)acetylacetonate	54	150	180
Magnesium 2,4-Pentadionate	87	95	270
Manganese naphthenate	69	360	590
Nickel acetylacetonate	51	170	170
Stannous octoate	97	310	1730
Ti ethyl acetoacetate chelate	50	340	Gelled
Ti acetylacetonate chelate	72	300	Gelled
Ti triethanolamine chelate	—	Gelled	
Zinc acetate	>200	210	Gelled
Zinc acetylacetonate	197	270	570
Zinc di-2 ethylhexyldi-thio-phosphate	35	280	Gelled
Zinc nitrate	84	290	680
Zinc octoate	95	325	540
Zirconium 6-methylhexanedione	138	295	590
Zirconium octoate	—	Gelled	—
Zirconium(IV) trifluoroacetylacetone	72	120	145

Table 4—Viscosity of Carboxyl Functional Acrylic Resin in the Presence of 0.4% Zn

Counterion to Zinc, Acid	Viscosity, cps
Octanoic no Zn added (control)	880
Acetic	1480
Dichloro acetic acid	1160
Isobutyric acid	1440
Octanoic acid	1440
Maleic isobutyl half ester	1480
Benzoic acid	1240
2-(o-Toluoyl)benzoic acid	1520
Oxalic acid	1240
Ethylmalonic acid	1520
o-Phthalic acid	Precipitate, gel
Glycolic acid	Hazy precipitate
Lactic acid	1120
2-Hydroxyisobutyric acid	1120
2-Hydroxycaproic acid	1080
Citric acid	1000
o-Hydroxybenzoic acid	1240
Dodecylbenzene sulfonic acid	900
Zinc chelate with proprietary acid (ZnCH)	960


(14)

The reaction of epoxy groups with anhydride groups can be catalyzed by both acidic and basic catalysts yielding esters.[15] The reaction is catalyzed by water, hydroxyl, and carboxyl compounds, which leads to the following proposed mechanism[16]: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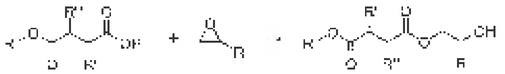
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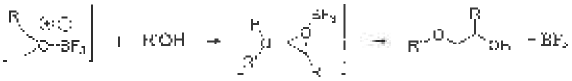
(17)

In the initial reaction step, the anhydride reacts under uncatalyzed conditions with the hydroxyl compound [equation (15)] forming a carboxylic acid, which in turn reacts with an epoxide [equation (16)]. It was also observed in this reaction that an excess of epoxy groups is consumed. Therefore, the catalysis of the hydroxyl-epoxy reaction [equation (17)] by anhydride was proposed.[17]

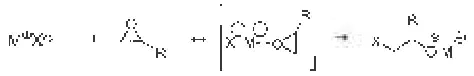
Cationic catalysts for epoxies also include Lewis acids.[18] Many inorganic salts such as halides of Al, B, Be, Fe(III),[19] Sb(V), Sn, Ti, Zr and Zn,[20,21] are included in this category as active catalysts.[22] Inactive as catalysts are the halides of As, Sb(III), Co, Cu, Fe(II), and Hg. The most common cationic catalyst used is boron trifluoride.[23] The reaction of epoxy groups in the presence of hydroxyl groups proceeds via a carbonium ion mechanism [equations (18 and (19)]. This reaction leads to the formation of ether linkages and is, therefore, not very desirable as a catalyst for the epoxy-carboxyl or anhydride reaction.


(18)


(19)

Metal catalysts (such as metal alkoxides[24]), metal chelates (such as dionate complexes) and metal oxides (such as barium oxide or strontium oxide), have been used as anionic catalysts.[25] Some of the aluminum alkyl compounds can be considered coordination catalysts, producing very high molecular weight polyether homopolymers. An exact mechanism[26] for this type of catalyst is not known.

Polymerization with metal oxides typically involves the coordination of the metal with the epoxy group, leading to reaction with another epoxy group.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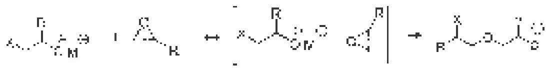
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EXPERIMENTAL

As substrates for the crosslinking reaction, we selected commercial polymers having both glycidyl ether and glycidyl ester functionality. The glycidyl ether resins were bisphenol A diglycidyl ether resins. The glycidyl ester resins were glycidyl methacrylate functional acrylic resins. We used acrylic copolymers as the carboxyl functional resins. The glycidyl ester functional resins were powder-coating polymers. The crosslinking studies were conducted on coatings prepared from solutions. We selected a wide range of commercially available amine catalysts for this study. The catalysts were selected based on pKa value and literature reports of activity as a catalyst for the epoxy-carboxyl reaction. Wherever possible, we used commercially available metal salt catalysts or salts available from the chemical supply houses without further purification. We followed the literature examples for the preparation of a large variety of experimental metal salt catalysts. These metal salts were prepared either in water or in a solvent by combining a stoichiometric amount of an oxide, hydroxide, carbonate, or alkoxide with the acid. The compositions of the salts were determined by pH, ICP, or X-ray analyses.

A special synthetic route was developed for a very effective zinc chelate now commercially available (ZnCH).[27] Despite its very ionic nature, this zinc compound has very good solubility in aliphatic and aromatic hydrocarbons and in nonpo-

Table 5—Cure Response and Stability of Glycidyl Ester and Carboxyl Functional Acrylic Resin in the Presence of 0.24 % Zn (as Salt) and 0.48% Ethylimidazole

Cure Conditions Test	140°C, 15 min MEK Double Rubs	150°C, 15 min MEK Double Rubs	Stability at 50°C, Gel Time, Days
Uncatalyzed	60	180	10
Zinc chelate with proprietary acid (ZnCH)	140	>200	6
2 Ethylimidazole	140	>200	3.5

Table 6—Cure Response of Carboxyl Functional Polyester and Bisphenol A Diglycidyl Ether, 0.25% of Zn or 0.005% of Amine Catalyst

Catalyst	MEK Double Rubs	
	150°C, 20 min	220°C, 20 min
No catalyst	30	70
ZnCH	140	190
Tetrabutylphosphonium bromide	135	190
1H-Imidazole, 4,5-dihydro-2-phenyl	145	195

Table 7—Stability of Carboxyl Functional Polyester and Bisphenol A Diglycidyl Ether, 0.25% of Zn or 0.005% of Amine Catalyst

Catalyst	Viscosity Stability	
	Initial Viscosity, cps	1 Week at 50°C, cps
No catalyst	96	136
ZnCH	104	178
Tetrabutylphosphonium bromide	112	550
1H-Imidazole, 4,5-dihydro-2-phenyl	100	336

lar solvents. Addition of very low amounts of polar solvents has a pronounced effect on the viscosity and solubility of this catalyst.

RESULTS

A commercially available glycidyl ester functional acrylic resin[28] was dissolved in n-butyl acetate and blended at a 1:1 molar ratio with a commercially available carboxyl functional acrylic resin[29] that was dissolved in methoxypropylacetate.

This formulation was catalyzed with various commercially available amine catalysts at a catalyst concentration of 0.005 mol% based on the total resin solids. The coating was drawn down on steel panels pretreated with iron phosphate at a dry film thickness of 1 mil (25 microns). The high molecular weight of these coating polymers precluded the measurement of film hardness as an indication of cure.

The uncatalyzed formulation requires a cure schedule of 160°C for 20 min to reach 200 MEK double rubs of solvent resistance. For a cure schedule of 15 min, the cure temperature has to be increased to 170°C to achieve 200 MEK solvent double rubs. It is probably not correct to call such a system uncatalyzed, since the free carboxyl groups provide some catalysis for this coating. The results are shown in *Figure* 1.

At a cure temperature of 110°C, the uncatalyzed and most of the catalyzed formulations did not show any indication of cure (*Table* 1). Only the quaternary ammonium compounds showed an improvement in methyl ethyl ketone (MEK) resistance. At the 140°C cure schedule, there is some indication of cure with the uncatalyzed formulation. None of the primary amines nor the phosphonium compound gave any cure improvement at this temperature. A "proton sponge," (N,N,N',N'-Tetramethyl-1,8-diaminonaphthalene) was also ineffective as a catalyst. Tertiary amines and imidazoles showed activity at 140°C. Strongly basic quaternary ammonium compounds were the most effective catalysts at this temperature. The viscosity stability of the catalysts was also measured at room temperature for seven weeks. All of the amine catalysts, which showed any indication of being effective catalysts at 140°C, gelled during the seven week aging test. The formulation containing the quaternary ammonium compound had gelled after only two weeks.

We tested all of the amine catalysts with acceptable cure response for overbake yellowing and humidity resistance. (*Table* 2) Tetrabutylammonium hydroxide and tetramethylguanidine showed acceptable yellowing under these cure conditions. The quaternary ammonium hydroxides gave the best cure response, but they were deficient in water humidity resistance.

The same glycidyl ester and carboxyl functional acrylics used in the amine catalyst study were catalyzed with different metal salts (*Table* 3). The metal catalysts were compared on an equal metal concentration of 0.28% of metal based on the resin solids. Because of the poor solubility of some of the metal salts and chelates, some of them required the addition of propylene carbonate as a solvent. The addition of a metal carboxylate to the carboxyl functional resin presented an immediate problem for many of the salts, either resulting in precipitation or gelation. Most of the metal carboxylate catalyzed formulations were hazy due to local precipitation of the polymer-carboxyl salt. The viscosity increase seen at room temperature aging was a result of ionic interaction between the anion and the

Table 8—Cure Response and Resistance Properties of Carboxyl Functional Acrylic and Bisphenol A Diglycidyl Resin Cured Six Minutes at 204°C

Catalyst	Catalyst wt%	Pendulum Hardness (sec)	Flexibility T-Bend	Cleveland Condensing Humidity 45°C 168 hr Gloss 20°, %	Boiling Water Test 60 Min Appearance after Test
No catalyst	0	141	>5	(b)	Destroyed
ZnCH	0.25	187	>5	(b)	Destroyed
ZnCH	0.5	194	0	95	No change
ZnCH	1.0	193	0	97	No change
ZnCH	2.0	203	0	95	No change
2-Ethylimidazole	0.5	191	0	98	No change
Amine ADMA-10	0.5	190	>5	43	Microblister
Phosphonium salt[a]	0.5	187	0	90	No change

(a) ETPI is an ethyl triphenyl phosphonium iodide catalyst.
(b) Failed humidity test after 48 hr

Table 9—Stability of Carboxyl Functional Acrylic and Bisphenol A Diglycidyl Resin at 25°C and 50°C

	Catalyst Level, wt%	Viscosity, ICI 25°C, Poise 4 Weeks at Room Temperature	Viscosity, ICI 25°C, Poise 3 Weeks at 50°C
No catalyst	0	1.15	1.75
ZnCH	0.5	1.15	2.5
ZnCH	1.0	1.9	2.5
ZnCH	2.0	1.9	3.7
2-Ethylimidazole	0.5	4.7	gelled after 4.5 days
Amine ADMA-10	0.5	3.7	gelled after 8.5 days
Phosphonium salt	0.5	3.5	gelled after 5.5 days

carboxyl groups leading to ionic crosslinking. Some of the metal chelates did not show this increase in viscosity. Only some of the zinc compounds gave complete cure and more than 200 MEK rubs.

To further elucidate the effect of the zinc counterions on solubility and interaction with the carboxyl groups of the acrylic resin, zinc salts of different acids were prepared. The test solution was prepared with a commercially available acrylic resin with a carboxyl equivalent weight of 748. Fifty parts by weight of this resin were dissolved in 50 parts by weight of 2-methoxypropyl acetate and the catalyst was dissolved in 3.5 parts by weight of methanol. A concentration of catalyst was used which corresponded to 0.4% of zinc based on the weight of the acrylic polymer. The viscosity of the blend was immediately measured. Exchange of the zinc salt with the carboxyl groups of the resin can lead to ionic crosslinking and to an increase in viscosity [equation (22)].

$$2RCO_2H + Zn(R'CO_2)_2 \leftrightarrow (RCO_2)_2Zn + 2R'CO_2H \quad (22)$$

We observed that the hydroxy acids and the acids with a higher pKa showed a reduced increase in viscosity. Zinc sulfonic acid salts gave excellent stability, but poor cure response (*Table* 4).

One of the zinc salts chelated with a proprietary acid[31] (ZnCH) exhibited a minimal viscosity increase. A formulation was prepared comparing the ZnCH catalyst and 2-ethylimidazole as a catalyst. The catalyst levels were adjusted for the ZnCH and imidazole to give the same cure response at 140°C. A level of 0.24% of zinc and 0.48% of 2-ethylimidazole based on the resin solids was required. The results of the cure study are shown below in *Table* 5 and indicate an improvement in formulation stability for the ZnCH catalyst in comparison to the imidazole catalyst.

The ZnCH catalyst was further tested in a model formulation based on a carboxyl functional polyester[32] for powder coating and a liquid diglycidylether of bisphenol A.[33] This formulation served as a typical compound for a powder coating. The molar ratio of carboxyl to epoxy groups was 1:1 in the formulation. The ZnCH was used as a catalyst at a concentration of 0.25% Zn (0.0038 mol%) based on total binder. For comparison, an imidazole and a phosphonium catalyst were used at the recommended concentration of the manufacturer of 0.005 mol% on resin solids. The formulations were formulated at an epoxy to carboxyl ratio of 1:1.

The results of the cure test and stability are shown in *Tables* 6 and 7. The cure responses at 140° and 220°C are equivalent for both formulations. The ZnCH catalyzed formulations show superior viscosity stability at 50°C.

A coating was formulated using an experimental carboxyl functional acrylic polymer with an equivalent weight of 1150 and a bisphenol A diglycidyl resin.[34] The ratio of carboxyl to epoxy used was 1:1. As solvent, a mixture of Aromatic 100 and 2-methoxypropyl acetate was used. The formulation was tested uncatalyzed and with different concentrations of ZnCH. For comparison with 2-ethylimidazole, dodecyldimethylamine (Amine ADMA-10) and tetrabutylphosphonium bromide were used as catalysts. Applications were made on tin free steel at a dry film thickness of 0.15 mil and cured six minutes at 400°F (204°C). The results are reported in *Table* 8. All of the formulations gave good cure response, as measured by hardness development. The flexibility and humidity resistance of the uncatalyzed formulation and the formulation catalyzed with 0.25% of the ZnCH (0.025% Zn) were deficient. The ADMA-10 amine catalyzed formulation had poor flexibility and showed blistering in the humidity test, indicating poor cure or a lack of adhesion. The ZnCH catalyst showed good performance over the wide range of

Table 10—Formulation of Carboxyl Acrylic and Bisphenol A Diglycidyl Resin

	Parts by weight
Grind:	
Acrylic resin, carboxyl functional, 75.8% (nonvolatile in xylene/n-butanol) Equivalent weight on solids = 1150	8.6
2-Methoxypropyl acetate	14.0
Aromatic 150 solvent	1.4
Ti-pure R-900 rutile titanium dioxide[35]	28.4
Let Down:	
Acrylic resin, carboxyl functional, equivalent weight on solids = 1150 75.8% (nonvolatile in xylene/n-butanol)	20.3
Epon 1001 bisphenol epoxy resin (100% solids EW= 538)	12.8
2-Methoxy propyl acetate	14.3
Flow and leveling agent	0.2
Catalyst	varies
Total	100

Table 11—Film Properties of Carboxyl Acrylic and Bisphenol A Diglycidyl Resin

Catalyst	Catalyst Level, %	Gloss 20, %	Gloss 60, %	Pendulum Hardness (sec)	Flexibility T-bend
No catalyst	0	60	76	115	>5
ZnCH	0.56	65	80	140	>6
ZnCH	0.85	70	80	132	0
ZnCH	1.28	75	90	152	0
ZnCH	1.70	83	94	162	0
ZnCH	2.00	83	95	163	0
2-Ethylimidazole	0.85	82	92	152	0
Amine ADMA-10	0.85	78	92	140	4
Phosphonium salt	0.85	85	95	140	0

Table 12—Film Properties of Carboxyl Acrylic and Bisphenol A Diglycidyl Resin

Catalyst	Catalyst Level. %	Gloss 20, %	Gloss 60, %	Pendulum Hardness (sec)	Impact Resistance Direct/Reverse in./lb
ZnCH	0.85	90	95	129	60/<5
ZnCH	1.70	90	97	129	110 / 20
ZnCH	2.00	91	96	130	160/130
2-Ethylimidazole	0.85	90	96	140	160/160
Amine ADMA-10	0.85	85	95	122	60/<5
Phosphonium salt ETPPI	0.85	78	93	130	60/<5

catalyst concentrations 0.5 to 2.0% (0.05-0.2% Zn based on resin solids).

The formulations were tested for stability at room temperature and at 50°C. The amine and phosphonium catalyzed formulations gelled at 50°C in 4.5-8.5 days (*Table* 9). The ZnCH catalyzed formulations showed an increase in viscosity after three weeks at 50°C, but did not gel.

A titanium dioxide pigmented formulation was prepared. The epoxy resin was a bisphenol A diglycidyl ether resin with a molecular weight of approximately 1050 and the acrylic was a carboxyl functional resin with an equivalent weight of 1150. The formulation is shown in *Table* 10.

This formulation was applied over tin-free steel at a film thickness of 0.2 mil (5 micron) and cured at 204°C (400°F) for six minutes. With the exception of the uncatalyzed formulation and the formulation catalyzed with ZnCH at the lowest 0.56% (Zn 0.056%) level, all formulations gave adequate solvent resistance. The impact of the uncatalyzed formulation and the formulation with the ZnCH catalyst at the lowest level gave poor T-bend flexibility. The formulation with the ADMA-10 catalyst also gave a poor T-bend, presumably due to poor adhesion. The results are shown in *Table* 11.

The formulations were also applied on cold-rolled, degreased steel panels at a film thickness of 1.0 mil (25 micron) and cured for six minutes at 204°C, (400°F). The results are shown in *Table* 12. The yellowing results of these formulations are shown in *Table* 13. The ZnCH catalyzed formulations show no yellowing at any of the catalyst levels tested. The 2-ethylimidazole is most prone to yellow, the ADMA-10 shows only slight to no yellowing, and the phosphonium catalyst yellows slightly.

Catalysis of Epoxy Groups with Anhydrides

To demonstrate the catalytic activity of the ZnCH catalyst, a casting was prepared from a liquid bisphenol A diglycidyl ether resin and methyl tetrahydrophthalic anhydride (100/80). The formulations were catalyzed with 0.5% of ZnCH catalyst and 2-ethylimidazole, respectively. The ZnCH catalyzed formulation not only shows a superior potlife, but also does not yellow under the cure conditions shown in *Table* 14.

The use of epoxidized oils as crosslinkers for high-solids coatings is very attractive. To illustrate the catalysis of the reaction of anhydrides and carboxyl groups with an epoxidized oil, we crosslinked trimellitic anhydride with epoxidized soybean oil. Twenty-five parts by weight of a trimellitic anhydride and 75 parts by weight of an epoxidized soybean oil,[26] epoxy equivalent weight of 228, were dissolved in acetone. The formulation was catalyzed with 1.5% of catalyst based on the resin weight. The for-

Table 13—Yellowing Carboxyl Acrylic and Bisphenol A Diglycidyl Resin

Catalyst	Catalyst Level, %	b* Value after Cure at 400°F for 6 min
ZnCH	0.85	1.71
ZnCH	1.70	-1.70
ZnCH	2.00	1.70
2-Ethylimidazole	0.85	2.26
Amine ADMA 10	0.85	-1.13
Phosphonium salt	0.85	-0.18

b* refers to the yellow index of the CIELAB Color Model. This model is the second of two systems adopted by CIE in 1976 as models that better show uniform color spacing in their values. CIELAB is an opponent color system based on the earlier (1942) system of Richard Hunter called L, a, b. Color opposition correlates with discoveries in the mid 1960s that somewhere between the optical nerve and the brain, retinal color stimuli are translated into distinctions between light and dark, red and green, and blue and yellow. CIELAB indicates these values with three axes: L*, a*, and b*. (The full nomenclature is 1976 CIE L*a*b* Space.) See also reference 25.

Table 14—Anhydride Cure of Bisphenol A Diglycidyl Resin

	ZnCH	2-Ethylimidazole	Uncatalyzed
Original viscosity, cps, 25°C	900	900	900
Viscosity after 24 hr, cps, 25°C	900	4,200	900
Potlife, 25°C, days	>Two weeks	Three days	>Two weeks
Cure cycle: 1 hr at 80°C then 3 hr at 150°C			
Hardness, Shore D	95	95	Liquid
Yellowing of casting at the cure temperature			

Table 15—Anhydride Cure of Epoxidized Soybean Oil

	ZnCH	2-Ethylimidazole	No catalyst
Gloss 20°/60°, %	100/100	100/100	100/100
Pencil hardness	HB	2B	4B
Direct impact resistance, in./lb	100	5	0

mulation had a nonvolatile content of 83% and a viscosity of 900 cps. The coating was applied on iron-phosphated, cold-rolled, steel panels at a dry film thickness of 1.0 mil (25 microns) and cured for 20 min at 140°C. The results are shown in *Table* 15.

CONCLUSIONS

Base catalysis of glycidyl groups with carboxyl groups is very effective. The reaction proceeds at a low temperature, which leads to coatings which have limited stability at room or elevated temperatures. By reducing the basicity of the amine or using amine salts, it is possible to improve the stability of amine catalyzed coatings. Other potential catalysts are the quaternary ammonium and phosphonium salts, however amine, quaternary ammonium, and phosphonium catalyzed coatings have a tendency to yellow on overbake. The strong basicity of these catalysts also can lead to humidity resistance problems.

Metal salts can be used as catalysts for the epoxy-carboxyl reaction. The alkali salts of weak acids are also potential catalysts. The introduction of an alkali salt leads to water sensitive coatings. Zinc salts have been used in powder coatings as catalysts and as flatting agents. It has been recognized that zinc carboxylates are effective catalysts for the epoxy-carboxyl reaction. The divalent nature of the zinc can result in ionic crosslinking that again leads to instability, viscosity increase, and gelation. We found that it is possible, with the choice of the right counterion, to overcome ionic crosslinking and develop coatings that are stable at room and elevated temperatures.

We attribute the excellent stability of formulations containing the ZnCH catalyst to its lack of dissociation at low temperatures. As shown in equation (23), at room temperature a formulation containing the ZnCH catalyst does not favor an exchange of the ZnA compound with the carboxyl groups. Therefore, this does not lead to ionic crosslinking in the solution and to an increase in viscosity. At higher temperatures there is a faster exchange, although the equilibrium is still shifted to the left side of equation equation (24).

$$2R'CO_2H + ZnA \leftarrow (R'CO_2)_2Zn + 2HA \qquad (23)$$

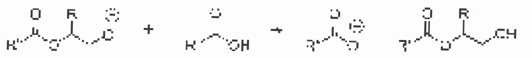
$$2R'CO_2H + ZnA \leftrightarrow (R'CO_2)_2Zn + 2HA \qquad (24)$$

At higher temperatures there is some reaction of the free HA with epoxy groups [equation (25)], shifting the equilibrium [equation (24)] to more $(R'CO_2)_2Zn$. Zinc will function as a base and form [equation (26)] a carboxyl anion that can lead to an attack of the epoxy group [equation (27)]. To disprove that the reaction of the zinc is not Lewis acid catalysis, we also prepared Zn sulfonate salts. These compounds are not effective catalysts for the epoxy-carboxyl reaction.


(25)

$$(R'CO_2)_2Zn \leftrightarrow 2\,R'CO_2^- + Zn^{++} \qquad (26)$$


(27)


(28)

We found zinc unique in effectively catalyzing the reaction of epoxy groups with carboxyl groups. By proper choice of the counterion, we were able to achieve good viscosity stability at lower temperatures and excellent cure at elevated temperatures.

The ZnCH catalyst has been shown to give excellent cure response combined with good stability, corrosion resistance and absence of yellowing.

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(27) NACURE® XC-9206 zinc chelate catalyst from King Industries, Norwalk, CT, Zn content 10 %, supplied in aliphatic hydrocarbon solvent.

(28) GMA 207-SA glycidyl functional acrylic polymer from Reichhold with an epoxy equivalent weight of 490 based on resin solids.

(29) Joncryl 819 acrylic polymer (Johnson Polymer) with a carboxyl equivalent weight of 748.

(30) b^* value (yellow index) measured with Minolta Spectrophotometer 508d according to CIELAB. CIE stands for Comission Internationale de l'Eclairage (International Commission on Illumination.) More information available from Color Vision Laboratory San Diego, www-cvrl.ucsd.edu.

(31) Mono and Di alkyl ester of a poly acid with pka values of between 2 and 13, respectively. He, Z.A., Blank, W.J., and Picci, M., U.S. Patent 6,335,304B1 (2002).

(32) Fine Clad M-8841 is a carboxyl functional polyester from Reichhold Chemical with an carboxyl equivalent weight of 1020.

(33) Epon 828 is a product of Resolution Performance Products, bisphenol A diglycidylether with an epoxy equivalent weight of 188.5.

(34) Epon 1001, available from Resolution Performance Products Co. (100 % solids, epoxy equivalent weight – 538).

(35) Ti-Pure R-900 a titanium dioxide pigment from E.I. DuPont de Nemours, Wilmington, DE.

(36) Vitroflex 7170 available from of Elf Atochem, (oxirane equivalent weight 228, oxirane content 7.0%).