Liquid, Sprayable, "Zero" VOC Coatings Utilizing Cycloaliphatic Epoxies

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Zero VOC, hazardous air pollutant free coatings formulations can be readily prepared from liquid cycloaliphatic epoxies and narrow polydispersity caprolactone polyols. These formulations can be applied by conventional spray equipment and are a viable liquid alternative to powder coatings. Using conventional liquid spray equipment, the capital investment for the installation of a new powder coating line can be avoided. With modification, these coatings can be diluted with water and thickened with conventional cellulosic thickeners used in waterborne coatings. In this study, we discuss the influence of key formulating variables like epoxy/hydroxyl mole ratio, catalyst concentration, polyol molecular weight, and polydispersity on coating properties. Viscosity reduction and sag resistance are also discussed.

INTRODUCTION

Cycloaliphatic epoxies differ from conventional diglycidylether of bisphenol-A resins in several ways: aliphatic backbone; react readily with acids but are essentially not reactive with typical amine/amide type conventional epoxy curing agents, no chlorine; viscosities of 350 cps versus 11,000 cps; and excellent weatherability.

The use of low viscosity cycloaliphatic epoxies has shown dramatic growth in cationic UV coatings. There are many publications on formulating and performance of these 100% solids 'zero' VOC coatings.[1-23] Less well documented is the use of cycloaliphatic epoxies in thermally cured coatings.[19,24-27] In principle, formulating know-how from UV cationic coatings could be applied to thermally cured systems. There are some differences, including the fact that UV coatings are usually not spray applied and thus can tolerate higher application viscosities than sprayed, thermally cured coatings. In baked cationic coatings, water can be used as a zero VOC diluent.

Caprolactone polyols have been shown to be effective reactive diluents for solvent-based[28] coatings and can speed the cure of cationic UV coating formulations. In cationic UV coatings, the OH groups of the polyol both speed cure and impart a certain cure sensitivity to humidity. In thermally cured coatings, there is no cure inhibition by humidity since the humidity inside an oven is very low. The enhanced water sorption brought on by polyol addition allows water to be used as a non VOC diluent in the coating formulation that contains both cycloaliphatic epoxies and polyols. These coatings are essentially high-solids organic coatings diluted with water. Water dilution has two benefits: low viscosity at zero VOC and the ability to use conventional, well-known strategies for imparting sag resistance and rheology control to waterborne coatings. Water uptake is limited due to the partial miscibility of the formulating ingredients with water. Care must be taken to avoid adding too much water causing phase separation.

Raw Materials

Cycloaliphatic Epoxies: A commercially available cycloaliphatic di-epoxy was used. The experimental tri- and tetrafunctional cycloaliphatic epoxies were prepared by a method described elsewhere.[29] Epoxy names are the approximate molecular weights of the unsaturated precursors of the cycloaliphatics epoxies; for example, epoxy 221. The number 221 is the molecular weight of the diene precursor used to make the epoxy. The diene is reacted with peracetic acid.

Caprolactone Polyols: Commercial polyols were used where noted. Experimental 150 equivalent weight di-, tri-, and tetrafunctional polyols were prepared in-house.

Viscosities, equivalent weight, water uptakes, and solids of the raw materials are shown in *Table* 1. Water

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Table 1—Raw Material Properties

Material	Viscosity, cps @ 25°C	Functionality	Equivalent Wt. Gm/Equiv	Water Uptake wt% 1 phase	Wt % Solids By ASTM 2369
Polyol 201[a]	400	2	270	13	98
Polyol 2XX	255	2	150	56	93
Polyol 303	1687	3	150	—	99
Polyol 421	2262	4	150	—	—
Polyol 301[b]	2250	3	100	33	97.3
Epoxy 221[c]	375	2	135	1.75	98.6
Epoxy 458	63000	3	180	—	—
Epoxy 568	Solid	4	179	—	—

(a) Union Carbide Tone 0201 or equivalent.
(b) Union Carbide Tone 0301 or equivalent.
(c) Union Carbide ERL-4221 or equivalent.

uptake was determined by titrating the material with distilled water until a cloud point (phase separation) was reached.

Starting Point Clear Formulation

In principle, the strong acid catalysts used here will allow the epoxy to readily react with any OH. Narrow polydispersity polyols made by ring opening polymerization generally have lower viscosities at a given molecular weight than condensation polyols. Thus, we used caprolactone polyols to give lower viscosity formulations. A starting point formula is given in *Table* 2. A key formulation parameter is epoxy/hydroxyl mole ratio, R. Coatings were cured 7 min at 121°C @ 0.8 mil DFT. The higher equivalent weight polyol results in softer coatings with R = 2.

Effect of Catalyst Level and R Value (Epoxy/Hydroxyl Mole Ratio) on Cure, Hardness, and Impact

A three variable, blocked, central composite 20 experimental design was run to define the 'cure' envelope. Variables were cure temperature (120°-180°C), catalyst level (0.5 to 2%), and R (epoxy/OH mole ratio, 1.25 to 12) using epoxy 221 and polyol 301. Dry film thicknesses were 0.7 to 0.8 mils. Coating formulation variables and performance results are in *Table* 3.

Table 2—Starting Point Cycloaliphatic Epoxy/ Caprolactone Polyol Coatings

Component	Formulation #1 Wt%	Formulation #2 Wt%
Epoxy 221	72.9	51.3
Polyol 201	—	47.5
Polyol 301	25.9	—
Catalyst[a]	0.9	0.9
Surfactant[b]	0.3	0.3
R	2	2
Hardness	3H	3B
MEK rubs	>200	>200
Impact F/R	72/28	100/52

(a) 3M FC-520 (di-ethyl ammonium triflate solution) or equivalent.
(b) OSi L-7604 or equivalent.

Design software allows the time to cure, t, to be calculated from the fitted formula (the data gave an excellent fit with an 'r-squared' statistic of 0.9949):

$$\begin{aligned}\ln(t) = {} & 1.25 - 0.88*[(\text{Temp} - 150)/30] \\ & -0.30*[(\ln(\text{Cat level }\%) + 0.02)/1.18] \\ & +0.076*[(\ln(R) - 1.35)/1.13] \\ & +0.23*\{[(\text{Temp}-150)/30]*[(\ln(\text{Cat level}\%) + 0.02)/1.18]\} \\ & +0.29*[(\text{Temp}-150)/30]^2\end{aligned}$$

Figures 1-5 are contour plots of time for cure as a function of catalyst level and cure temperature at different 'R' values (R = epoxy/OH mole ratios). The times to cure are on the contour. Higher catalyst levels and cure temperatures give faster cures, as expected. Higher 'R' values give slightly slower cure rates. If oven cure temperature and residence time is known, a formulator can choose the catalyst level and R value needed to fully cure.

Pencil hardness is mainly a function of epoxy/OH mole ratio (*Figure* 6). Higher R = higher hardness.

Reverse impact resistance is the inverse of hardness: more epoxy, less impact resistance (*Figure* 7). The key variable which controls reverse impact is R, epoxy/OH mole ratio.

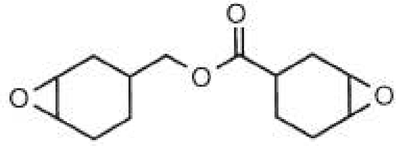
$$\begin{aligned}\ln(\text{reverse impact}) = {} & 0.76 - 2.383*[(\ln(R)-1.35)/1.13] \\ & +1.952*[(\ln(R) - 1.35)/1.13]^2\end{aligned}$$

Coil Coating Conditions

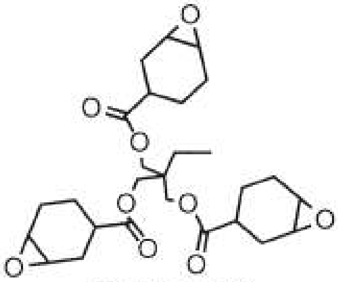
Other lab work suggests that coil coating cure rates can be attained by using >2% catalyst and baking to a peak metal temperature of 200°C (30-45 sec). Higher catalyst levels will speed cure. Triols and tetrols give faster cure with epoxy 221 under coil bake conditions.

Epoxy/Polyol Functionality

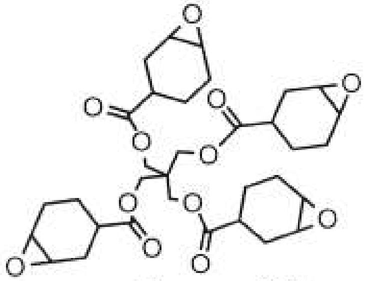
The influence of polyol and epoxy functionality was evaluated with a simple set of designed experiments. From previous work on thermally cured cationic coatings,[19,27] 0.3 to 2% catalyst was known to result in reasonable cure rates at 120°C and above with epoxy/hydroxyl mole ratios, R = 1.5. Design compositions, cure rates and coating properties are shown in *Table* 4. Each polyol had an equivalent weight of 150. Catalyst level was two percent. Dry film thicknesses were 0.7 to 0.8 mils. Coatings were cured at 120°C. Structures of the epoxies are shown in the following:



Epoxy 221



Epoxy 458



Epoxy 568

Shortest cure times (fastest cure rates) were found with the commercial di-epoxide reacted with tri and tetrafunctional polyols. The lowest viscosity was with the diol and diepoxy. Unexpectedly, experimental tri and tetrafunctional epoxies did not speed cure. They also had higher application viscosities. It is probable that the higher viscosities of epoxy 458 and 568 slowed cure due to diffusion effects on cure rate. All further work was carried out with the commercial diepoxy and a commercial diol or triol.

Corrosion Resistance

Since this technology uses a strong acid catalyst, one needs to evaluate the corrosion resistance requirements for metal substrates. *Table* 5 contains 300 hr salt spray data for several epoxy 221/polyol 301/0.5% catalyst clear coatings. Shorter cure times and higher epoxy levels reduce creepback at the scribe in ASTM B-177 salt spray tests. Clear coatings were drawn down to 1.5 mil DFTs on Bonderite 1000.

The use of anticorrosive pigments and additives will improve salt spray resistance.[24] The original formula in reference 24 did not include the acid catalyst and contained products not currently available, so the following modified formulas are suggested.

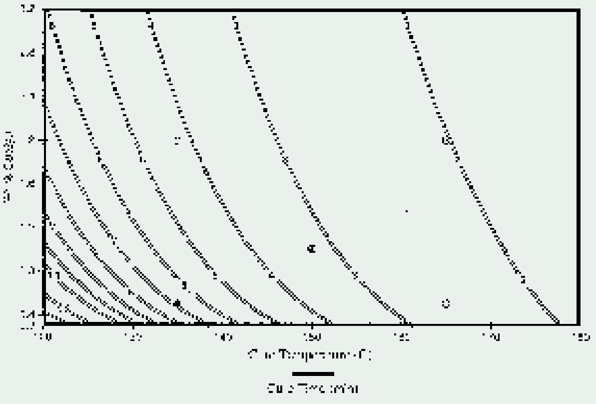


Figure 1—Epoxy/OH = 1.25.

Usually zinc phosphate is used in combination with the iron phosphate. The original authors[24] did not include the zinc in their formulations. We continue to study this issue.

Water Dilution

Model clear formulations were prepared with polyols 201, 301, and di-epoxy 221. These formulations were diluted with water and the viscosities were measured as a function of added water. Results are shown in *Figures* 1 and 2 for epoxy/hydroxyl mole ratios of 2 and 4, respectively. Obviously, water is an effective diluent for these 100% solids organic coatings. Added water had no effect on the cure rates.

Rheology Control of Water Diluted Systems

Cellulosic type thickeners are known to be effective in imparting sag control in waterborne coatings. It was not

Table 3—Three Variable Design on Cure Variables

Temp °C	Cat Wt%	Epoxy/OH	Time[a], min	Hardness	Impact F/R
135	0.5	2.0	5.75	2H	100/32
165	2.0	2.0	2.00	2H	100/40
165	0.5	8.0	2.75	3H	36/0
135	2.0	8.0	4.75	3H	24/0
150	1.0	4.0	3.50	2H	48/0
150	1.0	4.0	3.50	2H	40/2
165	0.5	2.0	2.50	2H	108/24
135	2.0	2.0	4.25	2H	92/24
135	0.5	8.0	7.50	3H	32/0
165	2.0	8.0	2.25	3H	44/0
150	1.0	4.0	3.50	2H	32/2
150	1.0	4.0	3.50	2H	40/2
120	1.0	4.0	11.25	H	44/8
180	1.0	4.0	2.00	3H	44/0
150	0.3	4.0	5.00	3H	48/0
150	3.2	4.0	2.75	2H	52/2
150	1.0	1.25	3.25	F	132/56
150	1.0	12	3.75	3H	28/2
150	1.0	4.0	3.5	2H	40/2
150	1.0	4.0	3.5	2H	48/0

(a) Cure time needed to reach 200+ MEK rubs.

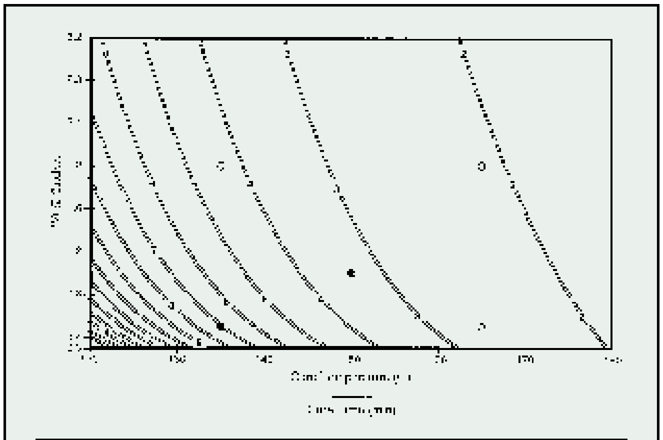


Figure 2—Epoxy/OH = 2.0.

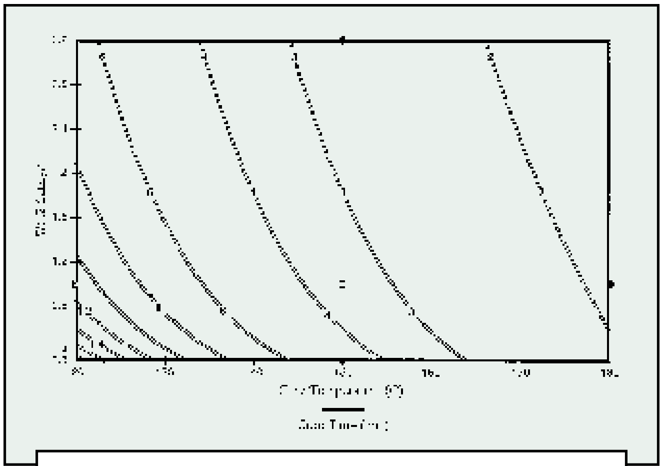


Figure 3—Epoxy/OH = 4.0.

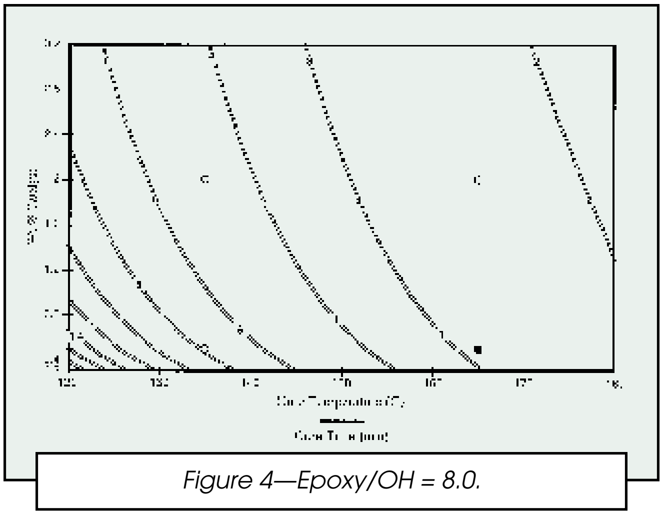


Figure 4—Epoxy/OH = 8.0.

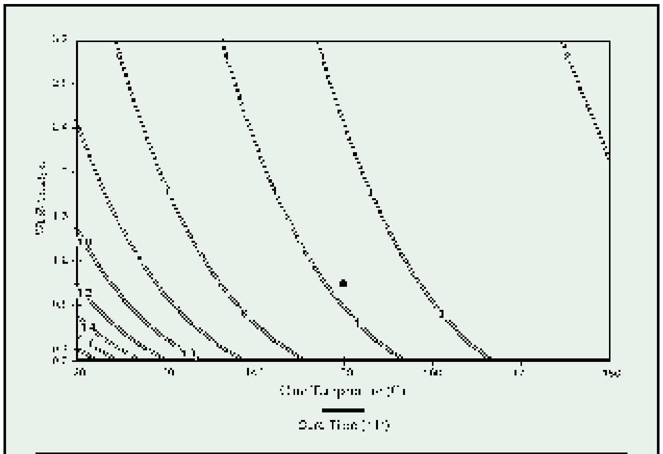


Figure 5—Epoxy/OH = 12.0.

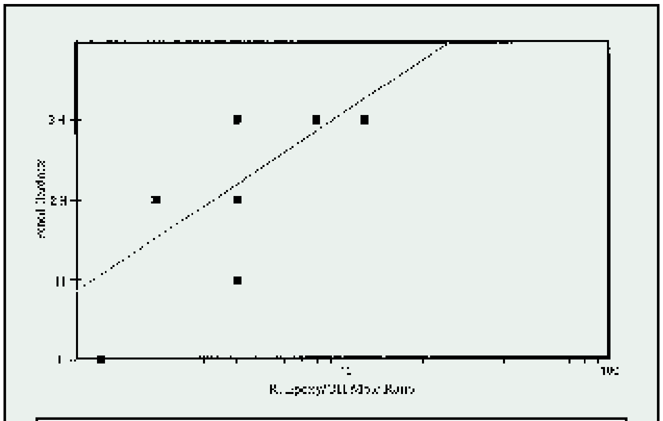


Figure 6—Hardness vs. Epoxy/OH.

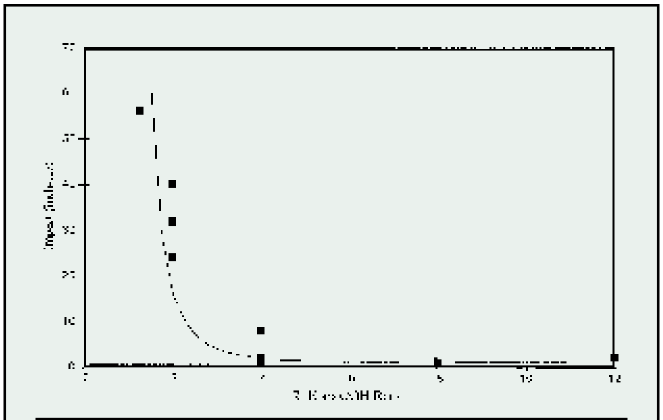


Figure 7—Reverse impact.

obvious that they would be effective in 100% solids, water diluted cycloaliphatic epoxy coatings. Initial work showed that water diluted 100% solids epoxies, thickened with a cellulosic thickener, exhibited shear thinning as measured on a Brookfield type viscometer. A variety of thickeners were evaluated. The thickener specified in *Table* 7 gave sag resistance. Other cellulosics and associative thickeners were not effective in this system. *Table* 7 contains a starting point water reduced, rheology modified formula along with coating performance data. Best coating appearance was observed with a spray gun heated at 40-60°C. Lower application temperatures produced more orange peel in the cured coating.

Lower Cure Temperatures

In the course of this work it was observed that the addition of lithium triflate (3M FC-122)[30] to the formulations discussed previously will reduce cure temperature to below 100°C. 0.25% lithium triflate will act as an effective catalyst, showing 40-50 MEK rubs vs. 0-15 for the blocked triflic acid (FC-520) when both systems are cured 40' @ 100°C in R = 2/triol formulations @ 0.25 to 0.4 mils DFT. Lithium triflate is lower in cost than the blocked acid (FC-520) on a cost/active # basis. The combination of the blocked triflic acid plus triflate is also effective.

Formulating Tips

- For cationic cure, all additives and rheology control agents must not contain basic substances, since bases will stop cationic cure. Basic pigments and amine treated pigments will inhibit cure. Basic rhodamine pigments will inhibit cationic cure. Basic pigments and additives cannot be used in cationically cured coatings. A list of cationic compatible pigments is available from the authors.

- Cure depends on loss of a small quantity of volatile amine blocking agent from the triflate catalyst (FC-520). If the coating is too thick or if the oven is not vented, the

Table 4—Experimental Design

Functionality (name)

Epoxy	Polyol	Cure[a] Time Sec	Pencil H	Viscosity CPS	Impact F/R
2 (221)	2 (2XX)	405	H	195	112/72
2 (221)	4 (421)	360	H	660	100/72
4 (568)	2 (2XX)	540	H	Paste[b]	88/94
4 (568)	4 (421)	555	H	Paste[b]	112/64
3 (458)	3 (303)	450	2H	4150	120/64
3 (458)	2 (2XX)	435	2H	1175	112/56
2 (221)	3 (303)	345	H	540	108/72

(a) Cure time to 200 MEK rubs.
(b) Semi-solid, thinned with solvent for coatings tests.

Table 5—Corrosion Resistance of Clear Coatings

Wt% Polyol	Epoxy/OH (mole ratio)	Cure Time (min)	Creepback (in.)
0	∞	9	0
0	∞	30	1/8
33	1.61	9	3/8
33	1.61	30	5/8
40	1.18	9	3/8
40	1.18	30	3/8

Table 6—Corrosion Resistant Formulations

Ingredient	Formulation #1 Wt%	Formulation #2 Wt%
Epoxy 221	68.85	63.00
Polyol 305	20.40	—
Polyol 201	—	26.75
Ferric Phosphate anti corrosive pigment	10.00	10.00
Coupling agent[a]	0.5	—
Catalyst[b]	0.25	0.25
Surfactant[c]		0.35

(a) Kenrich KR-55 or equivalent.
(a) 3M FC-520 or equivalent.
(b) OSi Silwet L-7500 or equivalent. (PO modified methylpolysiloxane).

Table 7—Sag Resistant Formulation

Ingredients	Wt. of Component in Formulation
Epoxy 221	45.73
Polyol 201	28.65
Catalyst[a]	1.13
Water	10.9
Cellulosic thickener[b] solution 5% solids in water	4.25=wt of 5% solution in water
PIgment[c]	8.06

Performance Parameters	Performance
Hardness	HB
Viscosity	200 cps @ 60°C
Impact F/R	120/108
Sag bar rating	5 mil gap max, no sag when vertical in oven at the cure temperature
Cure time/temp	2.5 min @ 204°C @ 1 mil DFT
R (epoxy/OH)	3
Gloss 60°/20°	84/70

(a) 3M FC-520 (diethylammonium triflate solution) or equivalent.
(b) Union Carbide Cellosize QP-300 or equivalent.
(c) Hoechst-Celanese, 13-3072 NovaPerm Red F2RK-70 ground with BYK P-104-S or equiv. ground for 7': 85% epoxy 221, 14% pigment, 1% P-104-S.

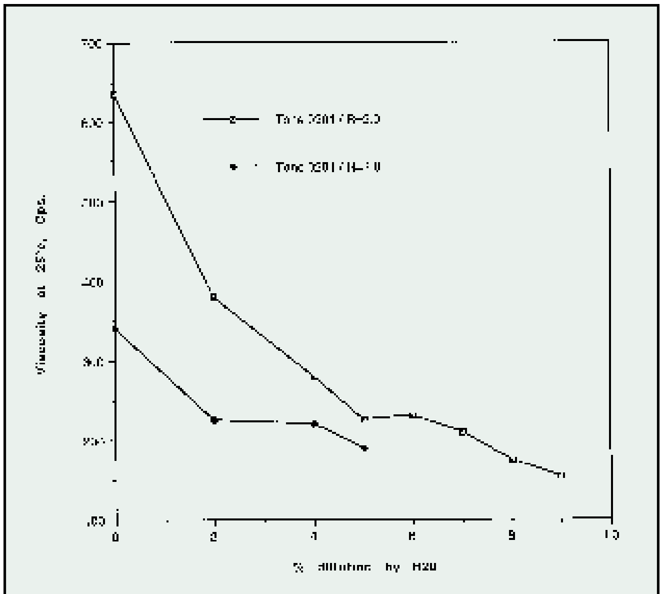


Figure 8—Effect of dilution by water on cycloaliphatic epoxy/polyol clearcoats. Epoxy/ hydroxy mole ratio = 2.0/

amine may not completely exit the film and cause cure inhibition. Lithium triflate (FC-122) has no volatile blockers.

- Viscosity increases with increasing polyol branching: diols make lower viscosity coatings than triol and tetrols. More epoxy (higher R values) is needed with diols to get hard coatings.
- High epoxy content (epoxy/hydroxyl mole ratio) increases corrosion resistance (*Table* 5).
- More catalyst increases cure rate but may hurt corrosion resistance.

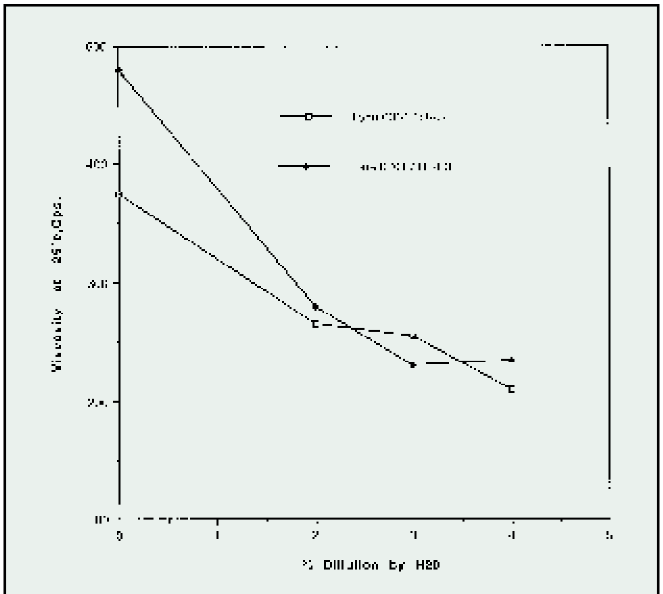


Figure 9—Effect of dilution by water on cycloaliphatic epoxy/polyol clearcoats. Epoxy/ hydroxy mole ratio = 4.0.

- Epoxy/hydroxyl mole ratio, R, has a large effect on impact resistance.

CONCLUSIONS

(1) Cycloaliphatic epoxies and caprolactone polyols can be formulated into low viscosity, low to 'zero' VOC coatings.

(2) These coatings can be diluted with water to sprayable viscosities.

(3) Cellulosic type thickeners are effective in imparting sag resistance to water-diluted 100% solids epoxy/ polyol formulations.

(4) Cure rates of these systems depend on several variables: epoxy/hydroxyl mole ratio, polyol and epoxy functionality, catalyst level, and cure temperature.

(5) Formulations are readily pigmented.

(6) Since these coatings are cationically cured, basic pigments and substrates will inhibit the cure.

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