Cationic, Thermally Cured Coatings Using Epoxidized Soybean Oil

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Cycloaliphatic epoxy resins are used in coatings and inks because of their exceptionally low viscosity and reactivity with a variety of co-reactants, thus permitting high-solids and zero VOC coatings. The low viscosity of epoxidized soybean oil (ESBO), its reactivity, and relatively low cost make it an inexpensive candidate co-resin in cationic thermally cured coatings and inks using blocked acid catalysts. Formulations with up to 40% ESBO in the epoxy resin blend were investigated. Blending of cycloaliphatic resin with 10% ESBO gave a bake coating with the same results as the standard formulation except pencil hardness was one unit lower when cured for 12 min at 120°C with a heat de-blocked catalyst. The hardness of coatings with ESBO is adjustable by changing the epoxy/polyol ratio, using harder polyols and harder epoxy resins.

INTRODUCTION

The use of epoxidized soybean oil (ESBO) as an epoxy resin in thermally cured bake coatings was investigated. Cycloaliphatic epoxy resins are currently used in these applications due to their low viscosity, ring structure for physical property development, and high reactivity with a variety of products.[1-3] A typical cycloaliphatic epoxy resin is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (*Figure* 1).

Dirlikov reported on the use of vernonia oil, a naturally occurring epoxidized triglyceride, and commercially epoxidized oils as reactive diluents in air-dry coatings.[4] Photoinitiated cationic polymerization of vernonia oil was reported recently by Crivello.[5] Photoinitiated cationic polymerization of epoxidized soybean oil was reported by the authors.[6] Cationic UV-cured formulations containing ESBO were somewhat slower reacting at room temperature than the formulations with cycloaliphatic resins and gave somewhat softer coatings. Formulations with 10-20% ESBO cured tack free in a matter of seconds at room temperature, had reasonable coating properties, and significant reductions in formulation raw material costs. One hundred percent soybean oil-based coatings (ESBO and soy polyol) were also cured with UV catalysis, but were slower curing at room temperature and gave soft 6B coatings.

Epoxidized soybean oil, owing to its low viscosity, commercial availability, low cost, and reactivity due to oxirane groups, is also an attractive option for use in high-solids, low/zero VOC thermally cured coatings. In a typical epoxidized soybean oil molecule 15% of the fatty acid fragments are saturated and, therefore, unreactive, 25% have one oxirane group, 51% have two oxirane groups, and 9% have three oxirane groups.[7] From this distribution, an average soy triglyceride molecule would have 4.62 oxirane groups. A representation of the molecule is shown in *Figure* 2.

Previous literature has shown that a superacid catalyst based on trifluoromethanesulphonic acid (CF_3SO_3H, triflic acid) can catalyze oxirane homopolymerization and oxirane copolymerization with hydroxyl-functional

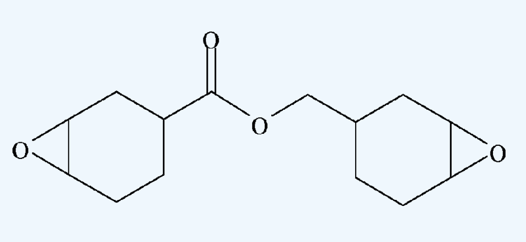

Figure 1—3,4-Epoxycyclohexyl-3,4-epoxycyclohexane carboxylate.

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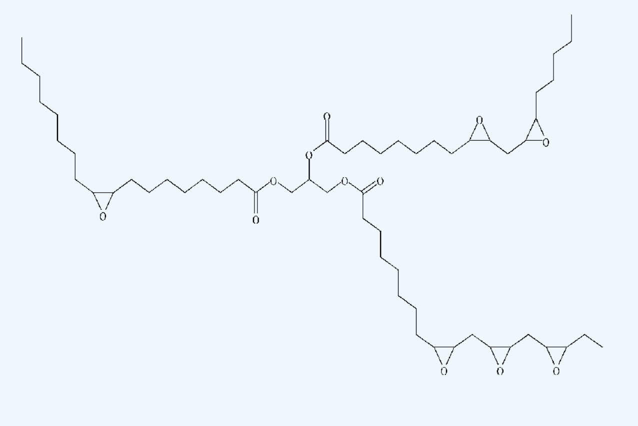


Figure 2—Epoxidized soybean oil.

oligomers, aminoplasts, and phenolics.[8,9] A proposed reaction mechanism for the system is shown in *Scheme* 1. The triflic acid protonates the oxirane oxygen followed by attack of a hydroxyl or an oxirane on the carbonium ion at C1 of the oxirane, generating another protonated species containing an ether on C1 and a secondary hydroxyl on C2 of the oxirane. The secondary hydroxyl can also propagate the polymerization, although at a slower rate than the primary hydroxyl of the polyol.[2]

A blocked acid catalyst is available in the form of an amine salt, $CF_3SO_3^{-}\ {}^{+}NEt_2H_2$, which de-blocks at elevated temperature to liberate the free acid with escape of the amine. Virtually any epoxy resin can be employed in a formulation with triflate catalysts. Selecting a liquid epoxy resin as the primary resin enables the formulation of very high-solids coatings. Coatings for various applications have been obtained based on cycloaliphatic epoxies, caprolactone polyols, and diglycidyl ether of bisphenol A.[2,3,10]

In this research, epoxidized soybean oil has been used as an additional resin co-reactant in blends with the commercial epoxy resins used in the bake systems described. A soy-based epoxy resin would be expected to impart flexibility and toughness to coatings based on the UV-cure data and earlier work introducing flexible aliphatic linkages into bisphenol A epoxy coatings.[6,11]

EXPERIMENTAL

Materials

Epoxy Resins: Vikoflex 7170, a fully epoxidized soybean oil (ESBO, EEW 231) and experimental 50% partially epoxidized soybean oil (ESBO50, EEW 458) were supplied by Elf Atochem, Inc. The cycloaliphatic epoxy resin Cyracure® UVR-6110 (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, Epoxy 1, EEW 136, also known as ERL-4221E), was supplied by Union Carbide Corp. Epoxy resin Epon® 828 (EEW 188), a diglycidyl ether of bisphenol A (DGEBA), was supplied by Shell Chemical Company. Epoxy novolac resin DEN® 439 (EEW 201) was supplied by Dow Chemical Company. Experimental resin trimethylolpropane triglycidylether (EEW 111) was obtained from a supplier who wishes to remain anonymous.

Polyols: Polyol Tone® 0301, a caprolactone triol (HEW 101), was supplied by Union Carbide Corp. Bisphenol A (HEW 114) was obtained from Aristech Chemical Corp. RJ-101, a styrene-allyl alcohol resinous polyol (HEW 118),was supplied by Monsanto. 4,8-Bis-(hydroxymethyl)-tricyclo [5.2.1.0^{2,6}]-decane (or dicyclopentadiene (DCPD) dimethylol, HEW 98) was obtained from Aldrich Chemical Co. The polyol of ESBO50 (from 50% epoxidized ESBO, HEW 130) was made by phosphorylation of ESBO50 with 1% by weight of 105% phosphoric acid followed by hydrolysis of the phosphate esters and oxirane groups with water.

Superacid Catalyst: Acid Catalyst, FC-520, an amine neutralized triflic acid was supplied by 3M Specialty Chemicals.

Additives: Fluorochemical surfactant FC-430 was supplied by 3M Specialty Chemicals and silicone surfactant OSi-L7604 was supplied by Witco.

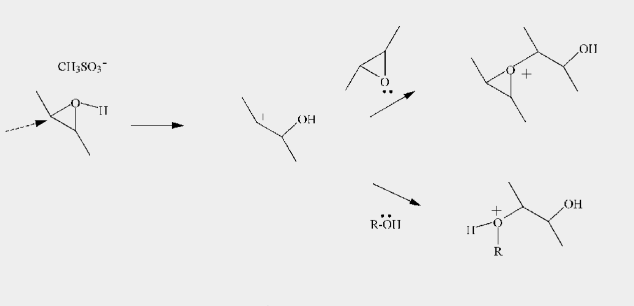
Other Chemicals: Melamine formaldehyde resin Resimene® 745 was supplied by Monsanto. Solvent methyl ethyl ketone was obtained from Aldrich Chemical Co.

Substrate: Iron phosphated steel panels of type R-36-I with a dull matte finish were obtained from Q-Panel Company. These iron phosphated panels had a coating weight of 40 to 60 mg/ft^2.

Testing Methods

The epoxide equivalent weight (EEW) of epoxidized oil and epoxy resin blends was determined by ASTM D 1652. The viscosity of the formulations was determined either by the Brookfield viscometer in accordance with ASTM D 2196 or by the ICI viscometer in accordance with ASTM D 4287. Percent nonvolatiles were determined by ASTM D 2369.

Cured film properties were determined 24 hr or more after thermal cure. Pencil hardness was determined by ASTM D 3363. Adhesion was determined by ASTM D 3359; impact resistance (forward/reverse) by ASTM D 2794; flexibility by ASTM D 522 (conical mandrel bend); solvent resistance by ASTM D 5402; and dry film thickness was determined with a Mikrotest magnetic coating thickness gauge.



Scheme 1

Table 1—Formulations with Varying Amounts of ESBO

	I	II	III	IV	V
Ratio of cycloaliphatic epoxy/ESBO	100	90/10	80/20	70/30	60/40
EEW of the epoxy resin blend	137	146	152	158	167
R = Epoxy equivalents / Hydroxyl equivalents	2	2	2	2	2
Component	**Parts by weight**				
Epoxy 1	73.78	67.04	60.48	53.64	46.15
ESBO	0	7.45	15.12	22.99	30.76
Polyol tone 0301	26.21	25.51	24.39	23.37	23.09
FC-520 (catalyst)	0.9	1.0	1.0	1.0	1.0
OSi L-7604 (surfactant)	0.3				0.3
FC-430 (surfactant)		0.3	0.3	0.3	
Brookfield viscosity (cPs, 25°C, 12 rpm)	499.9	432.4	427.4	474.9	567.4

Films were applied on the substrate with a wire-wound applicator rod #20 (DFT 0.7-0.9 mil) or rod #12 (DFT 0.3-0.4 mil).

RESULTS AND DISCUSSION

Epoxidized Soybean Oil Functionality: The molecular weight of epoxidized soybean oil is approximately 950 and the epoxide equivalent weight of our sample is 231, indicating that the average molecule in our sample of ESBO has about 4.2 oxirane groups. This is close to the theoretical value of 4.62 oxirane groups per molecule based on the typical fatty acid distribution of soybean oils. Statistically, most of the molecules will have between three and six oxirane groups. Only a small fraction of the oil would be expected to have zero to one oxirane groups per molecule. The reactivity of the oxirane groups in soybean oil is reasonably normal and the oxirane groups are measured satisfactorily by standard methods.

Effect of ESBO Concentration on Film Properties: Epoxidized soybean oil is an effective co-reactant that can be used in conjunction with cycloaliphatic epoxy resins for cationic cured systems. The coating property most affected by the use of ESBO is hardness, with the resulting films having lower pencil hardness due to the partial replacement of the rigid cycloaliphatic ring structure by flexible long-chain fatty acids in the triglyceride. The amount of ESBO was varied up to 40% of the total oxirane content (*Table* 1). The epoxide equivalent weight (EEW) of the epoxy resin blend was determined by titration and an epoxy/hydroxy equivalent ratio of 2 (R=2) was used in most of the experiments, where R is calculated by equation (1).

$$R = \frac{\text{Epoxy Equivalents}}{\text{Hydroxyl Equivalents}} = \frac{\text{g Epoxy / Epoxy Equivalent Wt}}{\text{g Polyol / Hydroxyl Equivalent Wt}} \quad (1)$$

A ladder study for curing indicated that 12 min at 120°F was optimum for this ESBO containing system (*Table* 2). The supplier of the cycloaliphatic epoxies reports that R is the key formulating parameter for ali-

Table 2—Film Properties of Formulation III (20% ESBO)

Bake Schedule	8 min/120°C	10 min/120°C	12 min/120°C	15 min/120°C
Pencil hardness (scratch/gouge)	B / H	B / H	F / H	F / H
Impact strength (F/R)	160/160	160/160	160/160	160/160
Adhesion	5B	5B	5B	5B
Flexibility	—	—	32%	32%
MEK double rubs	>200	>200	>200	>200
Film thickness (mils)	1.0	0.9 -1.0	0.9 -1.0	0.8 -1.0
Color and appearance	Colorless and glossy	Colorless and glossy	Colorless and glossy	Colorless and glossy

Table 3—Film Properties vs. ESBO Content

	I (Standard)	II (10% ESBO)	III (20% ESBO)	IV (30% ESBO)	V (40% ESBO)
Pencil Hardness (scratch/gouge)	H/4H	F/2H	F/H	HB/F	HB/F
Impact strength (F/R)	160 / 160	160/160	160/160	160/160	160/160
Adhesion	5B	5B	5B	5B	5B
Flexibility	32%	32%	32%	32%	32%
MEK double rubs	> 200	>200	>200	>200	160
Film thickness (mils)	0.8 - 0.9	0.9-1.0	0.9-1.0	0.9-1.0	0.7-0.8
Color and appearance	Colorless & glossy	Colorless & glossy	Colorless & glossy	Colorless & glossy	Colorless & glossy[a]

(a) Films are slightly rough; roughness increases if panel is not baked soon after drawdown.
Cure conditions: 12 min @ 120°C.

Table 4—Formulations with Increased R-Value

Formulation	VI	VII	VIII
Ratio of epoxy 1/ESBO	90/10	80/20	70/30
R = Epoxy equivalents / Hydroxyl equivalents	4	4	4
Component		**Parts by weight**	
Epoxy 1	76.85	68.7	60.47
ESBO	8.54	17.2	25.90
Polyol Tone 0301	14.61	14.1	13.62
FC-520 (catalyst)	1.0	1.0	1.0
FC-430 (surfactant)	0.3	0.3	0.3
Brookfield viscosity (in cPs) at 6 rpm and 24-25°C	414.9	459.9	394.9

phatic epoxy chemistry.[2] The weight of the polyol was calculated for R=2 making use of the EEW of the epoxies, the hydroxyl equivalent weight (HEW) of the polyols, and the weight of the epoxy resin blend used. The film properties were examined to determine the effect of various levels of epoxidized oil incorporated in a typical formulation. *Table* 3 lists the film properties of the formulations cured at 120°C for 12 min.

In general, the set of epoxy/polyol coatings possess excellent adhesion, flexibility, and impact resistance. The solvent resistance is >150 MEK double rubs up to the 40% oil level indicating that the ESBO is reacting into the binder. The pencil hardness is moderate and decreases with increasing amounts of epoxidized oil because of its long chain flexible structure (see *Figure* 2). At a bake schedule of 12 min/120°C, the coatings' seven-day pencil gouge hardness varies from 4H for the standard alkyd formulation to F for the formulation containing 40% ESBO. Introduction of 10% ESBO reduces the hardness from 4H to 2H; 20% oil gives a hardness of H. At 30% and 40% levels, the hardness is F. In addition, at the 40% level the films begin to become rough due to lack of homogeneity of the oil in the formulation. These results indicate that substitution of up to at least 30% of the total epoxy resin by ESBO can give smooth, glossy, colorless coatings with reasonable film properties.

EFFECT OF INCREASING R VALUE: Previous work on epoxy/polyol coatings showed that the higher the equivalent ratio R, the greater the film hardness.[2,6] To improve the hardness of these thermoset coatings, formulations with an R-value of 4 were examined where the amount of polyol in the formulation was calculated from the equivalents as described earlier. These formulations are shown in *Table* 4, and the film properties are listed in *Table* 5. The use of the inexpensive ESBO allows one to contemplate the use of higher R values to obtain hardness.

Comparing *Table* 3 formulation II film properties with *Table* 5 formulation VI film properties, we see that increasing R from 2 to 4 at the 10% oil level resulted in pencil gouge hardness increasing from 2H to 3H. This increase in hardness was accompanied by a considerable fall in the impact resistance, with other properties remaining unchanged. At the 20% ESBO level, the hardness remains the same for R=2 and 4, with the impact resistance remaining almost the same. At the 30% ESBO level, the hardness increases from F to H as R changes from 2 to 4, while the impact resistance remains the same. The system appears to be robust with considerable latitude in adjusting ESBO levels and R-values to obtain an economical formulation with a desirable set of coating variables. Pencil scratch hardness decreased with increasing R for formulations with greater than 10% ESBO.

Table 5—Film Properties of Formulations with R=4

	VI 10% ESBO	VII 20% ESBO	VIII 30% ESBO
Pencil Hardness (scratch/gouge)	H/3H	B/H	B/H
Impact strength (F/R)	35/5	150/150	160/160
Adhesion	5B	5B	5B
Flexibility	32%	32%	32%
MEK double rubs	> 200	>200	>200
Film thickness (mils)	0.9 - 1.0	0.8-1.2	1.0
Color and appearance	Colorless	Colorless	Golden

Cure conditions: 12 min @ 120°C.

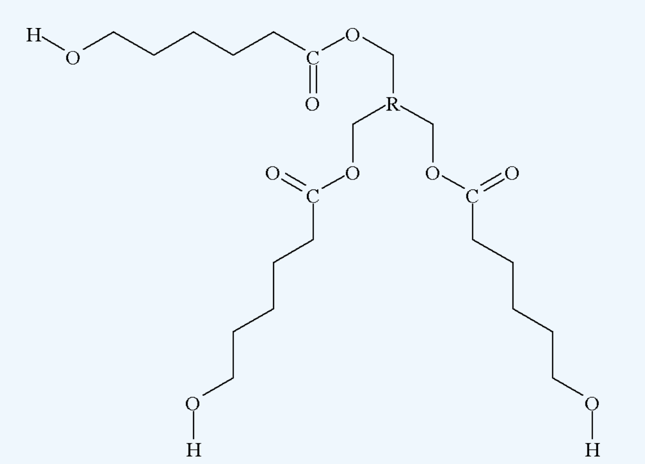


Figure 3—Tone polyol.

EFFECT OF OTHER COMPOUNDS IN IMPROVING HARDNESS: One way of altering the properties of the coatings under consideration is the use of other hydroxy compounds in place of the typically used polyols. In order to improve the hardness of the films, other hydroxy components were substituted in place of the Tone 0301 polyol (*Figure* 3).

Bisphenol A (*Figure* 4), owing to its rigid aromatic structure, was expected to improve the hardness.

Styrene-allyl alcohol copolymer (*Figure* 5) would also be expected to increase coating hardness because of the styrene ring structure.

4,8-Bis-(hydroxymethyl) tricyclo [5.2.1.0^{2,6}] decane (dicyclopentadiene dimethylol) (*Figure* 6) is another rigid molecule that would be expected to enhance coating hardness.

The use of a melamine-formaldehyde resin (*Figure* 7) as a hardener was tested in combination with Tone 0301 polyol. *Table* 6 summarizes the formulations containing these hardeners.

The R values for these formulations are high, that is, the amount of hydroxyl component used in the formulation is low in order to: (1) limit the amount of solvent (MEK) required to dissolve bisphenol A and RJ-101, which are solids, and (2) because larger amounts of a more rigid hydroxyl component would be expected to reduce the impact resistance of the coatings.

Table 6—Formulations with Various Polyol Hardeners

Formulation	IX	X	XI	XII
Ratio of Epoxy 1/ESBO	80/20	80/20	70/30	80/20
R = Epoxy equivalents / Hydroxyl equivalents	8	8	4	2
Component	**Weight, g**			
Epoxy 1	73.15	74	51.97	52.41
ESBO	18.29	18.5	22.27	13.10
Polyol Tone 0301				21.55
Bisphenol A	8.56			
Dicyclopentadiene dimethylol		7.4		
RJ-101			25.76	
Resimene 745				12.93
MEK	7.68		12	
FC-520	1.0	1.0	1.0	1.0
FC-430	0.4		0.3	0.3
OSi L-7604		0.5		
Viscosity (cPs)	380	420	460	504.9
Percent non-volatile content	93.8		89.4	

The pencil gouge hardness of formulation IX with bisphenol A and 20% ESBO matched the standard system with zero oil at 4H (*Table* 7). This increase in hardness was accompanied by a decrease in impact resistance (F/R) from 160/160 to 35/10. One might be able to optimize the bis A and ESBO to give a better set of properties with lower raw material costs. With dicyclopentadiene dimethylol as the hydroxy component, there was no change in film hardness at the 20% oil level, but there was a major decrease in impact resistance (*Table* 8). With styrene-allyl alcohol copolymer, at 30% oil level there was an increase of pencil gouge hardness to 2H, accompanied by a decrease in impact resistance (*Table* 9). The formulation with the styrene-allyl alcohol copolymer required more severe curing conditions. With the use of the melamine-formaldehyde resin at the 20% oil level, a substantial gain in hardness was not observed and the impact resistance decreased (*Table* 10).

USE OF OTHER EPOXY RESINS: Other epoxy resins were substituted for the cycloaliphatic epoxy resin in formulations XIII-XVIII shown in *Table* 11. DGEBA (*Figure* 8) is a less expensive, commodity epoxy resin with a rigid aromatic structure that would be expected to increase coating hardness.

Epoxy novolac resin would also be expected to help in improving hardness due to its rigid multifunctional aromatic structure (*Figure* 9).

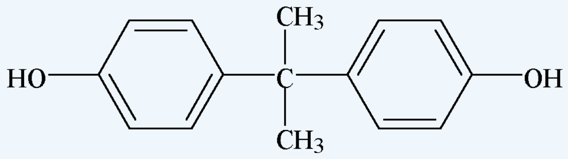


Figure 4—Bisphenol A.

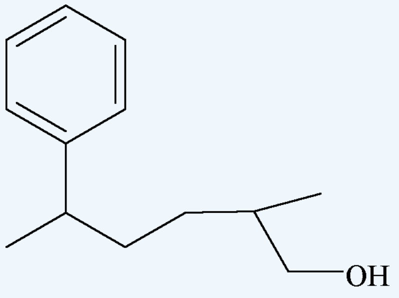


Figure 5—Styrene allyl alcohol copolymer.

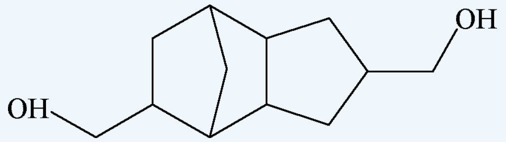


Figure 6—Dicyclopentadiene dimethylol.

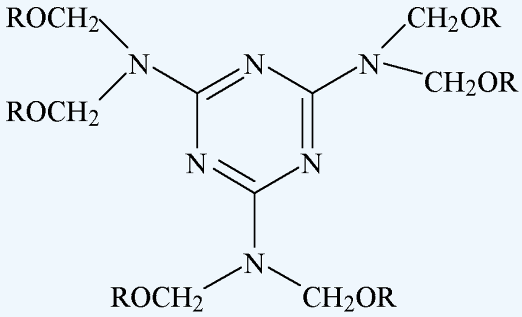


Figure 7—Melamine aminoplast.

Table 7—Film Properties of Formulation IX (Bisphenol A)

Bake schedule	10 min/130°C
Pencil hardness (scratch/gouge)	2H/4H
Impact strength (F/R)	35/10
Adhesion	5B
MEK double rubs	>200
Color and appearance	Colorless and glossy
Film thickness (mils)	0.9

Table 8—Film Properties of Formulation X (Dicyclopentadiene dimethylol)

Bake schedule	12 min/120°C
Pencil hardness (scratch/gouge)	F/H
Impact strength (F/R)	35/5
Adhesion	5B
MEK double rubs	>200
Color and appearance	Colorless and glossy
Film thickness (mils)	0.6-0.9

Table 9—Film Properties of Formulation XI (Styrene/allyl alcohol polyol)

Bake schedule	10 min/140°C
Pencil hardness (scratch/gouge)	F/2H
Impact strength (F/R)	55/30
Adhesion	5B
Flexibility	23%
MEK double rubs	>200
Film thickness (mils)	0.8-1.0
Color and appearance	Colorless and glossy

Table 10—Film Properties of Formulation XII (Polyol Tone 0301/ Melamine)

Bake schedule	12 min/120°C
Pencil hardness (scratch/gouge)	B/H
Impact strength (F/R)	55/25
Adhesion	5B
Flexibility	32%
MEK double rubs	>200
Film thickness (mils)	0.8
Color and appearance	Colorless and glossy

Table 11—Formulations Containing Other Epoxy Resins

Formulation	XIII	XIV	XV	XVI	XVII	XVIII
Epoxy1/Epoxy2/ ESBO	0/70/30	50/30/20	0/70/30	80/10/10	50/30/20	61/17/22
R = Epoxy equivalents / Hydroxyl equivalents	2	2	2	2	2	4.5
Component			**Parts by weight**			
Epoxy 1		38.42		59.16	37.05	52.4
Epoxy 2 Epon 828	55.7	23.06				
Epoxy 2 TMPTGE			51.68	7.4	22.23	
Epoxy 2 DEN 439						14.3
ESBO	23.9	15.36	22.15	7.4	14. 82	19.0
Polyol Tone 0301	20.4	23.15	26.17	26.04	25.90	14.3
FC-520	1.0	1.0	1.0	1.0	1.0	1.9
FC-430		0.3		0.3	0.3	
OSi L 7604	0.5		0.5			0.5
MEK		2.33				
Viscosity (cPs)	>1000	524.9	380	452.1	414.9	670

Table 12—Film Properties of Formulation XIII (70 DGEBA/30 ESBO)

Bake schedule	30 min/120°C + 30 min/140°C
Pencil hardness (scratch/gouge)	2B/HB
Impact strength (F/R)	160/160
Adhesion	5B
Double MEK rubs	>200
Film thickness (mils)	0.6-0.8
Color and appearance	Yellowish brown and glossy

Table 13—Film Properties of Formulation XIV (30 DGEBA Epoxy/ 20 ESBO)

Bake schedule	20 min/140°C
Pencil hardness (scratch H/gouge H)	HB/H
Impact strength (F/R)	160 /160
Adhesion	5B
Flexibility	ND
Double MEK rubs	> 200
Color and appearance	Yellow (golden) and glossy

Trimethylolpropane triglycidylether (*Figure* 10) is a triepoxide of lower molecular weight that was also tested for hardness improvement. The film properties of these formulations are shown in *Tables* 12-17.

Epoxy resins that contain glycidyl ethers are more sluggish in cationic cured formulations. All of the formulations with glycidyl ethers required more severe curing conditions than the cycloaliphatic epoxy formulations containing ESBO. Formulation XIII (*Table* 11), which contained no cycloaliphatic epoxy resin, only DGEBA epoxy resin and ESBO, required the most drastic conditions for cure (*Table* 12), and also exhibited strong yellowing. Formulation XV, also with no Epoxy 1, just TMPTGE and ESBO, also required stronger curing conditions (*Table 14*).

Formulation XIV, in which a portion of the cycloaliphatic epoxy resin has been replaced by DGEBA, showed no increase in pencil gouge hardness (*Table* 13) compared to Formulation III film properties (*Table* 2). Other properties measured were also the same, except for yellowing and more severe cure conditions for the bisphenol A system. The less expensive liquid DGEBA does not appear to be a particularly useful co-resin for increasing hardness of cationic cured cycloaliphatic/ESBO coatings in the formulations tested, since it consistently required harsher curing conditions and, as a result, gave yellowish coatings with little increase in film hardness.

The film properties for Formulation XVI (*Table* 15), with 10% ESBO, and 10% TMPTGE, remain almost the same as for the 90/10-cycloaliphatic epoxy/ESBO formulation (Formulation II, *Table* 2). With 30% TMPTGE and 20% ESBO, the film properties (*Table* 16) still remain the same as for Formulation III (*Table* 3). The shorter crosslink density expected of the TMPTGE did not result in harder coatings when used alone or as a diluent, perhaps because of the lower reactivity of the glycidyl ethers in cationic systems.

Seventeen percent epoxy novolac resin used in Formulation XVII with 22% ESBO (*Table* 17) does not appear to alter the film properties when compared with Formulation III at 20% oil level. This is consistent with data reported elsewhere.[2] There also appeared to be some incompatibility of the novolac and epoxidized oil as indicated by the uneven surface of the films.

Table 14—Film Properties of Formulation XV (70 TMPTGE/30 ESBO)

Bake schedule	15 min/120°C + 30 min /135°C
Color and appearance	Golden yellow and glossy
Pencil hardness	2B

Table 15—Film Properties of Formulation XVI (10 TMPTGE/10 ESBO)

Bake schedule	12 min/120°C
Pencil hardness (scratch H/gouge H)	F/H
Impact strength (F/R)	160/160
Adhesion	5B
Flexibility	≥ 32%
Double MEK rubs	> 200
Film thickness (mils)	0.8 - 0.9
Color and appearance	Colorless and glossy

Crosslinking with Soy Polyol: The polyol made from ESBO50 (*Figure* 11) was formulated with Epoxy 1 at a

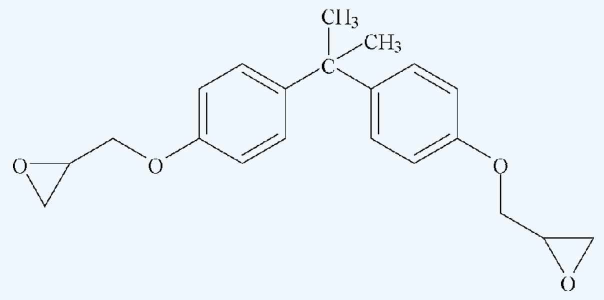


Figure 8—Diglycidylether bisphenol A.

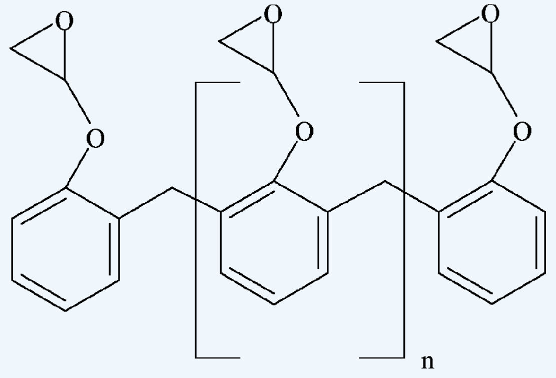


Figure 9—Epoxy novolac resin.

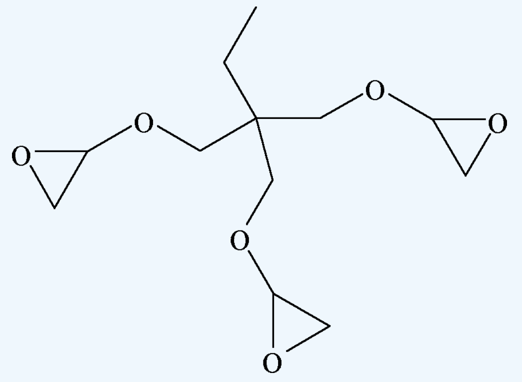


Figure 10—Trimethylolpropane triglycidyl ether.

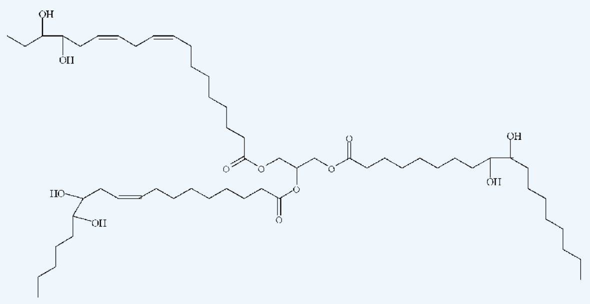


Figure 11—ESBO50 polyol.

60/40 ratio, R=1.5 (*Table* 18). The film properties that resulted are shown in *Table* 19. The coating had a pencil gouge hardness rating of B while the other properties measured were excellent, including MEK resistance (*Table* 2).

CONCLUSIONS

High-solids thermally cured coatings based on cycloaliphatic epoxy resin, epoxidized soybean oil, and polyols gave useful film properties as general-purpose coatings. The hardness of the films decreases with the increase of epoxidized oil (at constant R-value) without loss in the other properties measured. Inexpensive, epoxidized soybean oil can be used as a 10-20% partial replacement for commercial cycloaliphatic epoxy resins to give coatings with acceptable hardness. In coating applications where flexibility, impact strength, and adhesion are the major requirements as compared to hardness, up to 40% ESBO can be substituted for the cycloaliphatic epoxy resin. A 10-40% replacement of the epoxy resin by ESBO corresponds to a $0.30/lb-$1.30/lb reduction in the cost of the coating. Coatings with increased epoxy content as compared to hydroxyl content (that is, with increased R) show a small gain in film hardness at R=4 as compared with R=2. However, this is accompanied by a decrease in the impact resistance at a 10% oil level. With 20% and 30% oil, the impact resistance does not suffer. Perhaps a further increase in R, as well as the amount of ESBO, may help in arriving at an optimum level of hardness and impact strength.

The coatings containing bisphenol A or styrene-allyl alcohol polyol as a crosslinker show an improvement in film hardness at the R values and oil levels used. However, this is accompanied by a considerable decrease in the impact resistance and flexibility. Increasing the oil level further may be useful in achieving a proper balance between hardness and flexibility/impact resistance. 4,8-Bis-(hydroxymethyl)-tricyclo [5.2.1.0^{2,6}] decane (dicyclopentadiene dimethylol) and Resimene 745 were not very beneficial as hardeners in the bake coatings studied.

Formulations containing other epoxy resins such as DGEBA, trimethylolpropane triglycidylether, and epoxy novolac resin, do not seem to have any major gain in coating hardness at the concentrations used. The less expensive commercial aromatic epoxy resins may replace a portion of the cycloaliphatic epoxy in order to curtail the overall cost of the coating without substantial loss in other properties.

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Table 16—Film Properties of Formulation XVII (30 TMPTGE/20 ESBO)

Bake schedule	12 min / 120°C
Pencil hardness	H
Impact strength (F/R)	160 / 160
Adhesion	5B
Flexibility	32%
Double MEK rubs	> 200
Film thickness (mils)	0.7 - 0.95
Color and appearance	Colorless and glossy

Table 17—Film Properties of Formulation XVIII (17 Novolac/22 ESBO)

Bake schedule	12 min/120°C
Pencil hardness (scratch/gouge)	B/H
Impact strength (F/R)	150/150
Flexibility	32 %
Adhesion	5B
Double MEK rubs	>200
Color and appearance	Colorless and glossy. Slightly uneven (bumps and sinks)
Film thickness (mils)	0.8-1.0

Table 18—Formulation XIX with ESBO50 Polyol

Formulation	
Ratio of Cycloaliphatic Epoxy / ESBO Polyol, R=1.5	60/40
Component	**Parts by weight**
ERL 4221 E	60
ESBO50 Polyol	40
FC-520	1.0
OSi L 7604	0.5
Viscosity by ICI viscometer (cPs)	760

Table 19—Film Properties of Formulation XIX

Bake schedule	12 min/120°C
Pencil hardness (scratch/gouge)	2B/B
Impact strength (F/R)	160/160
Adhesion	5B
Flexibility	32%
Double MEK rubs	>200
Film thickness (mils)	0.7-0.9
Color and appearance	colorless and glossy

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