Waterborne Acrylic-Epoxy Coatings

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Waterborne two-component acrylic-epoxy coatings are gaining popularity as topcoats in moderate duty industrial and high performance architectural (HIPAC) applications. This increased popularity is due to their attractive handling, application, and performance properties, along with their low solvent content and odor. The objectives of this work were to characterize the cure and property development of these coatings, evaluate performance properties of cured films, and investigate a new epoxy resin dispersion in existing acrylic-epoxy formulations. These evaluations confirmed that existing acrylic-epoxy coatings have long pot life and short dry times while displaying a range of chemical resistance and physical properties. IR spectroscopy and differential scanning calorimetry (DSC) results indicated that the extent of cure at ambient conditions over a 21-day period was minimal; however, dynamic mechanical analysis (DMA) and solvent swell results did illustrate noticeable crosslink density development under these conditions. DSC results demonstrated more complete reaction and cure after heating. Direct substitution of a novel epoxy resin dispersion into these formulas resulted in lower required solvent content, shorter dry time, higher gloss, higher crosslink density, and improved water and scrub resistance.

INTRODUCTION

In the early 1990s, the drive for higher performance coatings with lower volatile organic compound (VOC) content led to the commercial introduction of waterborne acrylic-epoxy coatings. These are two-component coatings, with one component containing a carboxyl-functional acrylic latex, and the other component containing an epoxy emulsion. Upon mixing, cure is believed to proceed via carboxyl-epoxy reaction and/or epoxy homopolymerization. It is interesting that although these reactions usually proceed slowly under ambient conditions, the applied coating has attractive properties. The resulting crosslinked system is responsible for upgraded performance over acrylic latex coatings in properties such as hardness, mar, abrasion resistance, chemical resistance, and water resistance. These coatings also display faster dry and improved exterior durability over many epoxy-amine-based systems. Other attractive features include low organic solvent content and low odor. Therefore, acrylic-epoxy coatings are finding utility as topcoats in moderate duty industrial as well as high performance architectural applications. Examples of the latter applications are institutional (e.g., schools, locker areas, laboratories, etc.) wall surfaces of metal, masonry, plaster, and gypsum wallboard. References 1-5 provide additional information on the history, chemistry, and traditional performance of waterborne acrylic-epoxy coatings.

Both liquid epoxy resin emulsions and solid epoxy resin dispersions in water have been used to crosslink these systems. Liquid epoxy resins are lower molecular weight (i.e., < 1000) systems emulsified in water with the aid of a surfactant. Because of their relatively low molecular weight and viscosity, these systems exhibit good handling, flow, and coalescence, with little or no coalescing solvent; however, they usually take longer to dry, expecially dry hard. Solid epoxy dispersions are dispersed particles of higher molecular weight, solid epoxy resin in water. The molecular weight distribution of these resins is typically: 18% < 1000, 79% between 1000 and 10,000, and only 3% > 10,000. Coating systems with solid epoxy resin dispersions usually dry faster due to the lacquer dry of the higher molecular weight component, but they contain

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Table 1—General Comparison of Waterborne Epoxy Resins

General Properties	Liquid Epoxy Emulsion	Solid Epoxy Dispersion	New Waterborne Dispersion, AR-ER
Epoxy equivalent weight (on solids)	175-240	450-750	350
Supplied solids (%)	40-60	40-50	55
Solvent content (%)	0	10	0
Pot life	Short	Longer	Longer
Drying speed	Slow	Fast	Fast
Drying mechanism(s)	Chemical reaction	Lacqer dry and chemical reaction	Lacquer dry and chemical reaction

10% co-solvent to aid processing, assist flow, and permit coalescence of the film. From this description, the tradeoffs between liquid epoxy and solid epoxy resins in coating formulations are obvious.

A novel waterborne epoxy resin[6-8] has been developed which offers the most attractive features of both liquid and solid waterborne epoxy resin systems. This product will be designated AP-ER throughout this paper. The product is produced by emulsifying traditional Bisphenol A liquid epoxy resin, initiating homopolymerization, and stopping the polymerization when the desired degree of polymerization and molecular weight distribution has occurred. AP-ER epoxy resin has a unique molecular weight distribution that is quite different than both liquid and solid epoxy resins: 48% < 1000, 27% between 1000 and 10,000, and 25% > 10,000. This molecular weight distribution is responsible in part for its unique properties. The high molecular weight component of the material can allow for a fast, lacquer-type drying characteristic, while its low glass transition temperature (0°C) and minimum film formation temperature (4°C) allows fast dry with no co-solvent. *Table* 1 illustrates a general comparison of all three epoxy resin types. Previous research[7-8] with this new material primarily has been with amine-based cure systems; however, it would seem plausible that this resin may be suitable in acrylic-epoxy formulations. Potential advantages of this coating would include fast dry time and lower solvent content, while maintaining other performance properties. Therefore, the objectives of this project were:

(1) Characterize the properties and property development of commercial acrylic-epoxy coatings and published starting formulations.

(2) Study cure development of these coatings in relation to property development.

(3) Assess if and how the new epoxy resin may be used in waterborne acrylic-epoxy coatings.

Table 2—Parameters for Acrylic Resins Used in Starting Formulas

Property	Maincoat AE58[a]	Ecocryl 9790[b]
Solids content (%)	42.5	42.0
Water content (%)	57.5	43.5
Solvent content (%)	0	14.5
Density (lb/gal)	8.6	8.5
Viscosity (cP)	700	15,000
Equivalent weight (on solids)	1700	660

(a) Rohm and Haas
(b) Resolution

Table 3—Parameters for Epoxy Resins Used in Starting Formulas

Property	DC-9010W55[a]	Epi-Rez WD510[b]
Solids content (%)	55.0	100
Water content (%)	45.0	0
Density (lb/gal)	9.0	9.6
Viscosity (cP)	2000	10,000
Equivalent weight (on solids)	206	200

(a) Daubert
(b) Resolution

EXPERIMENTAL

Materials

Two commercially available acrylic-epoxy coatings were evaluated, along with two suggested starting formulas prepared within our laboratories. The commercial coatings are designated CC-1 and CC-2 while the control starting formulas are designated SF-1 and SF-2. *Tables* 2 and 3 list the properties of the acrylic and epoxy resins utilized in the published starting formulas that are listed in *Tables* 4 and 5. *Table* 6 lists formulation parameters of the coatings evaluated. It should be noted that CC-1 contains solid epoxy dispersion while CC-2, SF-1, and SF-2 contain liquid epoxy emulsion.

One objective of this work was to determine if and how the new epoxy resin may be used in waterborne acrylic-epoxy coatings. To pursue this objective, AP-ER was substituted at various concentrations into the CC-1 and SF-1 coatings for the standard epoxy resins in those systems. Since CC-1 is a commercial coating and little is known about the formulation other than the parameters listed in *Table* 6, mix ratios of CC-1 part A to AP-ER evaluated were 8:1, 4:1, and 2:1 by volume. Since the SF-1 formula was known (*Table* 4), AP-ER was substituted on a weight basis. Mix ratios of SF-1 part A to AP-ER were 905.5:41 g, 905.5:82 g, and 905.5:165 g, respectively. These substitutions were performed by simply making a direct replacement of the AP-ER for the existing epoxy component (part B) in each of the formulas.

Experimental Procedures

The coatings were mixed prior to application per the manufacturers' recommended procedures, including the suggested induction time of 30 min prior to application. The coatings were applied to cold rolled steel panels with zinc phosphate treatment (Bonderite 952) using a 6 mil bird bar. Free films were prepared by applying the coatings to a Tedlar film and then peeling the cured film from the Tedlar prior to testing. Unless otherwise noted, the

Table 4—Formula for SF-1

Ingredients	Pounds
Acrylic Component A	
Grind the following materials using a high-speed disperser for 20 min:	
Methyl Carbitol	38.8
Tamol 165 (Rohm and Haas)	13.8
NH_4OH (28% in water)	1.0
Triton CF-10 (Union Carbide)	1.6
Patcote 519 (Patco)	0.4
TiPure R-900 (DuPont)	193.7
Add the following and continue to grind for 2-3 minutes at lower speed:	
Water	19.9
Total Grind	**269.2**
Letdown Preparation	
Add the following in the order listed and mix thoroughly:	
Maincote AE-58 (Rohm and Haas)	493.0
Water	58.5
NH_4OH (28% in water)	2.4
Grind (from above)	269.2
Ektasolve EEH (Eastman Chemical)	48.2
Patcote 531 (Patco)	2.0
Water	14.2
Acrysol RM-1020 (Rohm and Haas)	8.0
QR-708 (Rohm and Haas)	1.2
Sodium Nitrite (15% aqueous solution)	8.8
Total Acrylic Component A	**905.5**
Epoxy Component B	
DC9010W55	**94.8**
Total Acrylic-Epoxy Topcoat	**1000.3**

Table 5—Formula for SF-2

Ingredients	Pounds
Acrylic Component A	
Water	66.60
Potassium tripolyphosphate (FMC)	1.82
Colloid 640 defoamer (Rhone-Poulenc)	1.82
Troton X-100 surfactant (Union Carbide)	1.82
Alcolec 439-C (American Lecithin Co.)	4.09
Ti-Pure R-702 (DuPont)	227.27
Eco-Cryl acrylic resin 9790 (Resolution)	98.18
High speed disperse to fineness of grind PC, then add	
Colloid 640 defoamer (Rhone-Poulenc)	1.82
Ektasolve EP (Eastman Chemical)	20.64
Eco-Cryl acrylic resin 9790 (Resolution)	367.27
Total Acrylic Component A	**851.88**
Epoxy Component B	
Sanduvor 3056 light stabilizer (Sandoz)	18.91
Ektasolve EP (Eastman Chemical)	16.18
Pre-mix the above, dissolve, then add:	
Epi-Rez WD-510 (Resolution)	61.82
Water	75.82
Total Epoxy Component B	**172.73**
Total Acrylic-Epoxy Topcoat	**1024.61**

applied coatings were allowed to cure for 21 days at 21°C, 50% relative humidity prior to testing. *Table* 7 lists the testing procedures that were followed to evaluate coating performance. Property development was characterized by assessing Persoz hardness and MEK double rubs as a function of time after application. ASTM D 3730 is a "Standard Guide for Testing High Performance Interior Architectural Wall Coatings (HIPAC)." This standard provides test methods and requirements for coatings used in these applications and was used as a guideline for the evaluation procedures and criteria.

In addition to coating property development on metal substrates, characterization of free films was performed 1, 7, 14, and 21 days after application to assess crosslink density, T_g development, and extent of cure. Cure development was studied via dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), IR spectroscopy, and solvent swells. DMA was performed using an RSA II from Rheometric Scientific. The specimen was tested in the tensile deformation mode at an applied frequency of one cycle/second over a temperature range of –100 to 200°C, heating in 6°C increments with a 60-sec soak time at each temperature to ensure isothermal conditions. The DSC analysis was performed using a 2920 DSC from TA Instruments heating from –130 to 250°C at a rate of 10°C/min. DSC data were analyzed using Universal V2.5H software from TA instruments. Gas flow rates were 50 ml/min of dry nitrogen and 25 ml/min of helium. Sample sizes were 10-20 mg. Samples were scanned, cooled, and then rescanned to determine the extent of cure. IR spectra were obtained using a Nicolet Magna 860 at 4 wavenumbers resolution with 128 signal average scans. A Fresnel ATR accessory from CIC Photonics was attached and the coatings were applied to an Amtir 1 ATR crystal.

Solvent swells were performed on free film samples approximately 2 cm by 2 cm by 40 microns. The test was performed by immersing the free film samples in MEK for one hour and, immediately upon removal, measuring the increase in length of the sides. These data were used to calculate a percent volume increase, which in turn was used to calculate a theoretical crosslink density. Crosslink density was calculated in terms of Mc, molecular weight between crosslinks, using the following equation:

$$Mc = \frac{\rho}{\nu_e} = \frac{V_o}{\nu_e'} = \frac{(\nu_2^{0.33} - \nu_2/2)}{-(\ln(1-\nu_2) + \nu_2 + \chi \nu_2^2)/\nu_1}$$

where: ρ is the polymer density assumed to be 1.0 g/ml, ν_e is the crosslink density in moles/ml, ν_e' is the moles of elastically effective network chains in volume V_o of unswollen polymer film, ν_1 is the molar volume of solvent (90.1 ml/mole for MEK), χ is the Flory-Huggins interaction parameter of solvent with network polymer (estimated to be 0.5 for this system), and ν_2 is the volume fraction of polymer in the swollen film at equilibrium swelling as mathematically defined by:

$$\nu_2 = 1/(1+f)^3 \text{ and } f = (x_2 - x_1)/x_1$$

where x_1 is the original length of a side of the polymer film (before swelling) and x_2 is the length after swelling.[9] The crosslink density was calculated from DMA data by:

Table 6—Formulation Parameters of Waterborne Acrylic-Epoxy Coatings

	CC-1	CC-2	SF-1	SF-2
Volume solids (%)	39	44	34	34
VOC (g/L)	209	230	230	230

Table 7—Procedures to Evaluate Coating Performance

Test of	HIPAC — (30-min Induction — 21 Day Cure)	ASTM Method
Substrate	Steel (cold rolled, Zinc Phos B952)	
Primer	None	
Application method	6-mil bird bar applicator	
Drying time (hr)	Set-to-touch	D 5895
	Tack-free	D 5895
	Dry-hard	D 5895
	Dry-through	D 5895
Film appearance	Gloss (20°)	D 523
	Gloss (60°)	D 523
	Gloss (85°)	D 523
Adhesion	Dry scrape (kg)	D 2197A
	Wet scrape (kg) (24 hr/ 21°C)	D 2197A
Immersion	Water immersion (24 hr/ 21°C)	
Solvent resistance	MEK double rubs	
	MEK immersion	
Spot tests	5% sol. Hydrochloric acid	D 1308
4-hr exposure	5% sol. Sodium hydroxide	D 1308
4-hr recovery	5% sol. Sulfuric acid	D 1308
	5% sol. Nitric acid	D 1308
	Chlorox	D 1308
	Mustard	D 1308
	Ketchup	D 1308
	Coffee	D 1308
	Lipstick	D 1308
Exposure	Humidity (1000 hr/38°C & 100% RH)	D 4585
	Xenon arc 500 hr (ΔE/60°gloss retention - %)	G 26
Impact	Gardner impact (in./lb) Direct	D 2794
	Gardner impact (in./lb) Reverse	D 2794
Flexibility	Mandrel Bend	D 1737
Hardness	Pencil	D 3363
	Persoz	D 4366
Scrub resistance	Cycles to failure	D 2486
Abrasion resistance	Taber (1000 g, 1000 cycles, CS17) mg. loss	D 1044

$$Mc = \frac{\rho}{\nu_e} = \frac{3RT}{E'}$$

where R is the ideal gas constant, and E′ is the modulus of the film at temperature T (100°C).

RESULTS

Benchmark Evaluations

The benchmarking results comparing the two commercial paints and two control formulas are presented in *Table* 8.

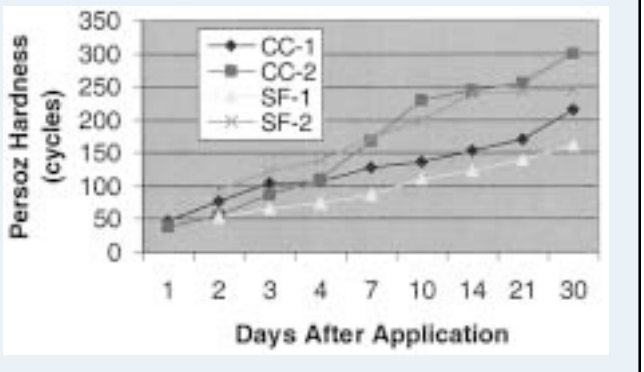


Figure 1—Development of Persoz hardness.

Several properties are notable for the entire group of four coatings. Generally, they display:

- — Long pot life (24-36 hr)
- — Short dry time (Set-to-touch in 15-45 min, Dry hard in 2-5 hr)
- — Good chemical resistance (200 MEK double rubs, four-hour chemical spot tests)
- — Fairly good hardness (Pencil hardness HB-H, Persoz hardness 142-249)
- — Fairly good weather resistance (500 hr Xenon arc Weatherometer with $\Delta E < 2$, 60° gloss retention of 68-98%)

With some of the other properties evaluated, a range of performance was observed between the four coatings. SF-1 withstood a 24-hr water immersion with no dramatic changes, while the other three coatings displayed blistering. After 1000 hours' exposure in a Cleveland Humidity cabinet, CC-1 and SF-1 had no obvious effects, while the other two coatings displayed blistering after only 24 hr of exposure. SF-1 had a direct impact flexibility of >160 in.-lb, while the other coatings had impacts of <30 in.-lb. Finally, scrub resistance ranged from 1924 cycles up to 4925 cycles, again illustrating a wide range of performance. Comparing these results with properties listed in ASTM D 3730, these coatings generally displayed moderate performance relative to industrial coating requirements and high performance relative to architectural applications, which suits their target markets and applications quite well as stated in the Introduction.

Substitution of the New Epoxy Resin into CC-1 and SF-1

One objective of this work was to determine if and how the new epoxy resin may be used in acrylic-epoxy coatings. To pursue this objective, the AP-ER resin was substituted at various concentrations into CC-1 and SF-1 as described in the Experimental section. The comparisons of the AP-ER substituted coatings versus those of the initial formulas CC-1 and SF-1 are reported in *Tables* 9 and 10, respectively. Substituting AP-ER into the CC-1 coating improved dry time, gloss, water resistance, and scrub resistance, with other properties generally remaining comparable. Dry hard times were reduced from 2.25 down to 0.75 hr, while dry through times decreased from 6.5 down to 3.5 hr. The dry through time for the coating at 4:2 AP-ER concentration was >12 hr probably due to excessive epoxy in the system, which does not harden. Gloss values of 60° increase from 66.5 up to the 85-90 range, another attractive feature for topcoat applications. AP-ER improved the 24-hr water immersion from blistering of the coating to virtually no effect on the coating or substrate. Finally, the scrub resistance was improved from 1924 up to the 5000 cycle range, again an attractive feature, especially for interior HIPAC topcoat applications. The SF-1 formulations with AP-ER similarly have decreased dry times and increased gloss. The decreased dry time with AP-ER could be expected due to its unique molecular weight distribution (described in the Introduction), which offers the coalescing attributes of liquid epoxy resin, while displaying the lacquer drying characteristics of solid epoxy dispersions without the need for co-solvent. The cause for improvements in gloss, water resistance, and scrub resistance is not quite as evident at this time. Further evidence may come from analytical studies presented and discussed later.

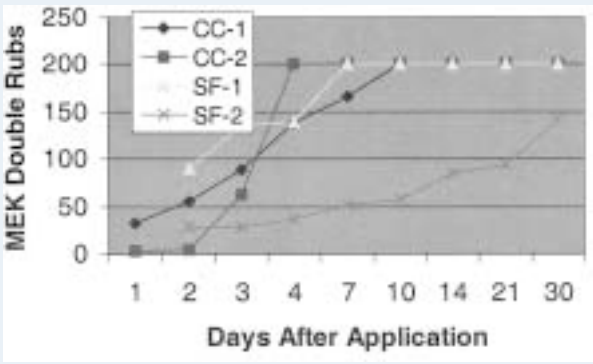


Figure 2—Development of MEK double rub resistance.

It should be noted that, in these studies, AP-ER was directly substituted for the epoxy component of CC-1 and SF-1 with no other adjustments to the formulation. Substi-

Table 8—Coating Benchmark Test Results

Test of	HIPAC — (1/2 hr Induction — 21 Day Cure)	CC-1	CC-2	SF-1	SF-2
Substrate	Steel cold rolled, Zinc Phos, B952				
Primer	None Color	White	White	White	White
	VOC (lb/gal)	1.50	2.13		
	Pot life/gel time	36 hr	24 hr	24 hr	24 hr
	Thickness (mils)	1.60	1.75	1.50	1.45
Drying time (hr)	Set-to-touch	<0.25	0.25	0.25	0.75
	Tack-free	0.50	0.50	0.50	1.25
	Dry-hard	2.25	4.75	2.00	2.25
	Dry-through	6.50	>12.0	4.25	5.75
Film appearance	Gloss (20°)	23.4	80.5	17.0	40.5
	Gloss (60°)	65.8	94.5	57.0	81.3
	Gloss (85°)	90.8	96.0	86.8	93.6
Adhesion	Dry scrape (kg)	>10.5	>10.5	>10.5	>10.5
	Wet scrape (kg) (24 hr/ 21°C)	>10.5	1.0	1.5	0.5
Immersion	Water immersion (24 hr/ 21°C)	Fail #8MD	Fail #8D	Pass	Fail #8D
	MEK immersion (1 hr/ 21°C)	Soft	Soft	Soft - Edge Lift	Swelled
Solvent resistance	MEK double rubs	Pass 200 Slight mar	Pass 200 Slight mar	Pass 200 Slight mar	Fail @ 93
Spot Tests	5% sol. Hydrochloric acid	No effect	No effect	No effect	No effect
4-hr exposure	5% sol. Sodium hydroxide	No effect	No effect	No effect	No effect
4 hr recovery	5% sol. Sulfuric acid	No effect	No effect	No effect	No effect
	5% sol. Nitric acid	No effect	No effect	No effect	No effect
	Chlorox	Stain	Stain	Stain	Stain
	Mustard	No effect	SLT Stain	No effect	No effect
	Ketcup	No effect	No effect	No effect	No effect
	Coffee	No effect	No effect	No effect	SLT Stain
	Lipstick	SLT Stain	No effect	Stain	Stain
Exposure	Humidity (1000 hr/38°C & 100% RH)	Pass	F@1day #6D	Pass	F@1day #8D
	Xenon arc 500 hr (ΔE)	1.2	0.21	1.47	1.75
	Xenon arc 500 hr (60°gloss retention - %)	87%	98%	81%	68%
Impact	Gardner impact (in./lb) Direct	28	24	160	12
	Gardner impact (in./lb) Reverse	<4	<4	160	<4
Flexibility	Mandrel bend	1/4"	5/8"	1/4"	1"
Hardness	Pencil	HB	H	H	HB
	Persoz	181	249	143	242
Scrub resistance	ASTM D 2486 (average cycles to failure)	1924	2565	4925	3425
Abrasion resistance	Taber (1000 g, 1000 cyc, CS17) mg. loss	175.0	157.0	193.8	228.6

Table 9—Coating Test Results for Substitution of New Epoxy Resin into CC-1

Test of	HIPAC — (1/2 hr Induction — 21 Day Cure)	CC-1	CC-1/AP-ER	CC-1/AP-ER	CC-1/AP-ER
Substrate	Steel cold rolled, Zinc Phos, B952		8:1 (volume)	4:1 (volume)	4:2 (volume)
Primer	None Color	White	White	White	White
	Pot life/gel time	36 hr			
	Thickness (mils)	1.60	1.98	1.75	2.20
Drying time (hr)	Set-to-touch	<0.25	0.25	<0.25	0.25
	Tack-free	0.50	0.50	0.75	0.75
	Dry-hard	2.25	0.75	1.00	1.75
	Dry-through	6.50	3.50	4.75	>12.00
Film appearance	Gloss (20°)	23.4	59.2	61.2	70.3
	GLoss (60°)	65.8	85.1	87.3	90.6
	Gloss (85°)	90.8	93.4	94.1	95.7
Adhesion	Dry scrape (kg)	>10.5	>10.5	>10.5	>10.5
	Wet scrape (kg) (24 hr/21°C)	>10.5	>10.5	>10.5	>10.5
Immersion	Water Immersion (24 hr/21°C)	Fail #8MD	Pass	Pass	Pass
	MEK Immersion (1 hr/RT)	Soft	Soft	Soft - Edge Lift	Soft
Solvent resistance	MEK double rubs	Pass 200 Slight mar	Pass 200 Slight mar	Pass 200 Slight mar	Pass 200 Slight mar
Spot tests	5% sol. Hydrochloric acid	No effect	No effect	No effect	No effect
4-hr exposure	5% sol. Sodium hydroxide	No effect	No effect	No effect	No effect
4-hr recovery	5% sol. Sulfuric acid	No effect	No effect	No effect	No effect
	5% sol. Nitric acid	No effect	No effect	No effect	No effect
	Chlorox	Stain	SLT stain	SLT stain	SLT stain
	Mustard	No effect	No effect	SLT stain	SLT stain
	Ketcup	No effect	No effect	No effect	No effect
	Coffee	No effect	No effect	No effect	No effect
	Lipstick	SLT stain	SLT stain	No effect	SLT stain
Exposure	Humidity (1000 hr/38°C & 100% RH)	Pass	Pass	Fail #8F day 13	Fail #8F day 13
	Xenon arc 500 hr (ΔE)	1.20	0.55	0.91	1.81
	Xenon arc 500 hr (60°gloss retention - %)	87%	83%	81%	74%
Impact	Gardner impact (in./lb) Direct	28	24	36	56
	Gardner impact (in./lb) Reverse	<4	<4	<4	4
Flexibility	Mandrel bend	1/4"	Pass @ 1/4"	Pass @ 1/4"	Pass @ 1/4"
Hardness	Pencil	HB	B	HB	3B
	Persoz	181	168	140	103
Scrub resistance	ASTM D 2486 (average cycles to failure)	1924	5250	5850	4600
Abrasion resistance	Taber (1000 g, 1000 cyc, CS17) mg. loss	175	185	236	241

tution of AP-ER in CC-1 resulted in a VOC reduction from 209 to approximately 180 g/L due to the elimination of solvent in the epoxy component. Good film formation was still observed. The acrylic component, having a high T_g, requires co-solvent or other means of plasticization to film form. We did not explore further VOC reduction by reformulating the acrylic component but this is a fertile area for additional investigation and development. It is possible that co-solvent levels in these systems, as in Part A of SF-1, and Parts A or B of SF-2 could be reduced when incorporating AP-ER, while obtaining good film formation.

Property and Cure Development

The development of Persoz hardness and resistance to MEK double rubs over the first 30 days after application are presented in *Table* 11 and illustrated in *Figures* 1 and 2. Hardness continues to increase steadily and considerably over this time period. The prolonged duration of hardness development may be due to the slow crosslinking reaction and/or the slow release of co-solvents. However, resistance to MEK develops at a faster rate, at least for coatings CC-1, CC-2, and SF-1, reaching 200 or greater double rubs within four to 10 days after application. This would suggest that crosslinking is developing, which is responsible for increased MEK resistance, while solvent release from the applied coatings is slow, thus causing the films to remain plasticized and soft. Considering the proposed crosslinking mechanisms of carboxyl-epoxy reaction and epoxy homopolymerization, both of which are slow at ambient conditions, it is surprising that MEK resistance develops this quickly. In order to assess the rate and extent of T_g and crosslink development, cure of SF-1 films was investigated using IR spectroscopy, DMA, DSC, and solvent swell up to 21 days after application.

The IR spectra of the SF-1 coating at 1, 7, 14, and 21 days after application are presented in *Figure* 3. These spectra show no obvious signs of reaction, including little, if any, epoxy decrease (epoxy band at 916 cm^{-1}) over this period. This is in contrast to the reported literature on these coatings,[1-5] which states that they will undergo carboxyl-epoxy reaction to develop crosslinking. However, as noted earlier, this reaction is very sluggish at room temperature and therefore these results may not be altogether surprising. Nonetheless, these results do seem to be in contrast to the ability of SF-1 to develop MEK resistance.

Table 12 lists results from the solvent swells, DMA and DSC characterizations and analysis for SF-1. During the first heating in DSC evaluations of the ambient cured SF-1 coatings (*Figure* 4A), a large exotherm was observed (noted as residual cure in *Table* 12), suggesting an incomplete cure under ambient conditions. The exotherm was ~30 J/g and it occurred between 80 and 200°C and stayed fairly constant in magnitude over the first 21 days after coating

Table 10—Coating Test Results for Substitution of New Epoxy Resin into SF-1

Test of	HIPAC—(1/2 hr Induction—21 Day Cure)	SF-1	SF-1 A: AP-ER	SF-1 A: AP-ER	SF-1 A; AP-ER
Substrate	Steel cold rolled, Zinc Phos, B952		905.5g/41g	905.5g/82g	905.5g/165g
Primer	None Color	White	White	White	White
	Pot life/gel time	24 hr			
	Thickness (mils)	1.50	2.12	2.03	2.61
Drying time (hr)	Set-to-touch	0.25	<0.25	<0.25	<0.25
	Tack-free	0.50	0.75	0.75	<0.25
	Dry-hard	2.00	1.25	1.25	0.75
	Dry-through	4.25	>12.0	>12.0	>12.0
Film appearance	GLoss (20°)	17.0	19.8	31.1	41.2
	Gloss (60°)	57.0	67.6	77.3	79.3
	Gloss (85°)	86.8	82.8	87.2	93.0
Adhesion	Dry scrape (kg)	>10.5	>10.5	>10.5	9.5
	Wet scrape (kg) (24 hr/21°C)	1.5	>10.5	>6	1.75
Immersion	Water immersion (24 hr/21°C)	Pass	Pass	Pass	Pass
	MEK immersion (1 hr/21°C)	Soft - Edge Lift	Soft	Soft - Edge Lift	Soft
Solvent resistance	MEK double rubs	Pass 200	Pass 200	Pass 200	Pass 200
		Slight mar	Slight mar	Slight mar	Slight mar
Spot tests	5% sol. Hydrochloric acid	No effect	No effect	No effect	No effect
4-hr exposure	5% sol. Sodium hydroxide	No effect	No effect	No effect	No effect
4-hr recovery	5% sol. Sulfuric acid	No effect	No effect	No effect	No effect
	5% sol. Nitric acid	No effect	No effect	No effect	No effect
	Chlorox	Stain	No effect	No effect	SLT Stain
	Mustard	No effect	No effect	No effect	No effect
	Ketcup	No effect	No effect	No effect	No effect
	Coffee	No effect			No effect
	Lipstick	Stain			SLT stain
Exposure	Humidity (1000 hr/38°C & 100% RH)	Pass			Pass
	Xenon arc 500 hr (ΔE)	1.47			1.56
	Xenon arc 500 hr (60°gloss retention - %)	81%			66%
Impact	Gardner impact (in./lb) Direct	160	160	56	72
	Gardner impact (in./lb) Reverse	160	32	4	<4
Flexibility	Mandrel bend	1/4"	1/8"	1/8"	1/8"
Hardness	Pencil	H	2H	H	H
	Persoz	143	142	139	114
Scrub resistance	ASTM D 2486 (average cycles to failure)	4925			
Abrasion resistance	Taber (1000 g, 1000 cyc, CS17) mg. loss	194			147

application. The T_g of the ambient cured material increased from 9 to 25°C over this 21-day period, as indicated by both DMA T_g onset results and DSC T_g midpoint results, which agree fairly well. After the first DSC heating, the SF-1 samples were cooled and then reheated in DSC (noted in *Table* 12 as second heat). During this second heating (*Figure* 4B), no residual exotherms were observed, the T_gs increased from the first heating, and the T_gs stabilized at ~40°C (i.e., they no longer were a function of the ambient cure time). To illustrate the cure during this first heating and the increase in T_g, *Figure* 4 illustrates the DSC scans for the first and second heating of SF-1 performed seven days after application. The DSC results indicate that the coatings did not reach their full potential cure under ambient conditions but were able to fully cure during their

Table 11—Coating Property Development

	Persoz Hardness			
	CC-1	CC-2	SF-1	SF-2
Day 1	47	38	—	—
2	76	56	54	93
3	103	88	65	120
4	107	110	75	138
7	127	168	86	172
10	136	230	110	197
14	152	243	122	238
21	169	255	140	242
30	215	299	161	245
MEK Double Rubs— (recorded @ failure up to 200)				
Day 1	32	3	—	—
2	55	5	90	28
3	89	63	135	28
4	138	200	140	37
7	165	200	200	51
10	200	200	200	57
14	200	200	200	84
21	200	200	200	93
30	200	200	200	141

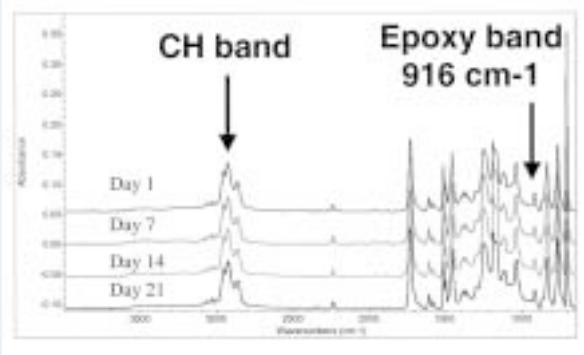
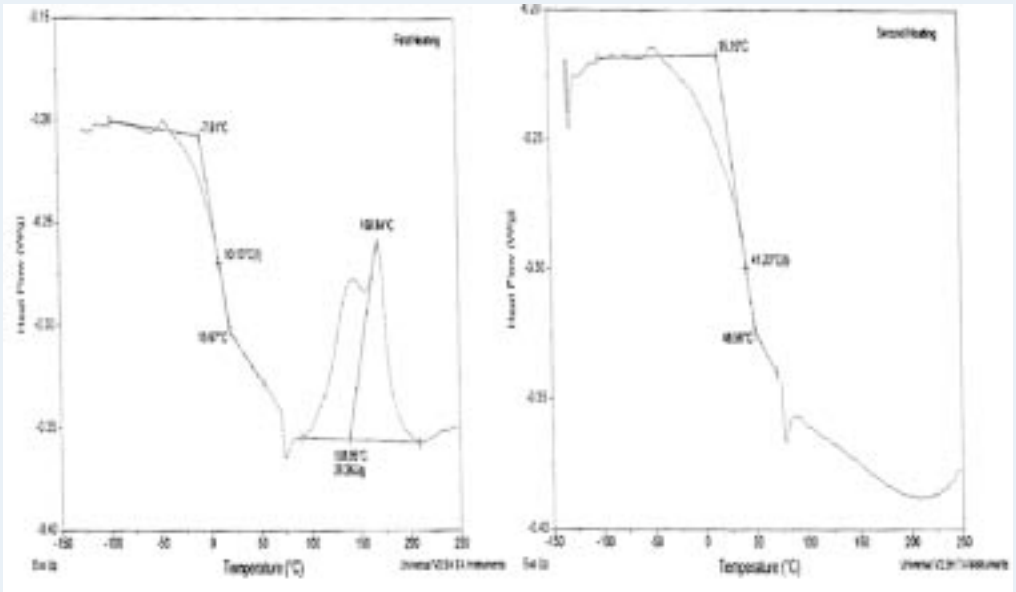


Figure 3—IR spectra of SF-1 coatings at 1, 7, 14, and 21 days after application.

Table 12—Cure Evaluations of SF-1 Coatings Using Solvent Swells, DMA, and DSC

Cure	Solvent Swell		DMA	DMA	DMA	DSC	DSC[a]	DSC[b]
Days	Vol % Increase	Mc Calc	Mc Calc	T_g Onset (°C)	T_g Mid (°C)	T_g Mid (°C)	Residual Cure	T_g Mid (°C)
		(g/mol)	(g/mol)				(J/g)	2nd Heat
1	125	171993	24492	5	33	9	35.5	37
7	82	27560	21402	15	40	10	28.3	41
14	80	25505	16723	25	46	17	26.3	41
21	91	43150	14907	25	46	25	27.3	43

(a) Determined as difference in exotherm observed from DSC scan during first heating minus exotherm observed from scan of second heating (no exotherm).
(b) T_g observed during second heating.



(A) First heating of SF-1 *(B) Second heating of SF-1*

Figure 4—DSC scans for the (A) first heating and (B) second heating of SF-1 performed seven days after application and cure at 21°C, 50% relative humidity.

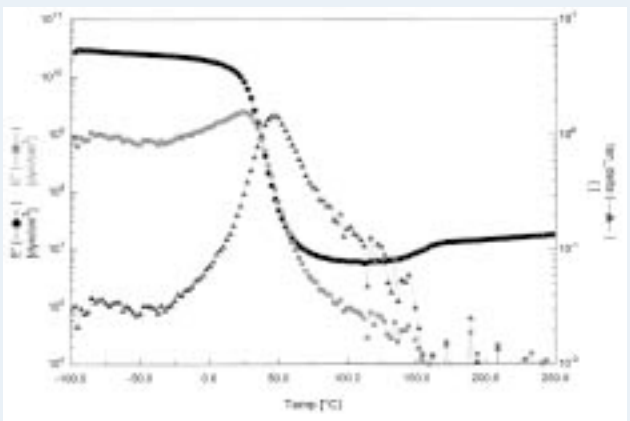


Figure 5—DMA results for SF-1 with AP-ER at a concentration of 905.5:165.

Table 13—T_g and Mc results from DMA analysis of CC-1 and SF-1 with AP-ER

Sample	DMA T_g Mid (°C)	Mc (g/mol)
CC-1 Part A:AP-ER; 2:1	56	5700
CC-1 Part A:AP-ER; 4:1	59	3400
SF-1	46	14907
SF-1 Part A:AP-ER; 905.5:41	58	2500
SF-1 Part A:AP-ER; 905.5:82	58	2100
SF-1 Part A:AP-ER; 905.5:165	58	2300

first DSC heating. It is likely that heating is required for these coatings to reach their maximum potential cure and crosslink density. The lack of incomplete cure at ambient conditions is most likely due to the naturally slow reaction of these systems at ambient conditions, combined with vitrification of the system at room temperature. However, it must be noted that only a small amount of chemical reaction is needed in thermosetting systems to achieve noticeable crosslink density of the system. These results illustrate that some crosslink density was achieved in these systems, evidently enough to impart a substantial level of chemical resistance and other properties (*Table* 8) required for them to perform adequately in their intended moderate duty industrial and high performance architectural applications.

Mc values (molecular weight between crosslinks) were calculated by applying the results of solvent swell and DMA analysis to the equations presented in the Experimental section. Lower Mc numbers indicate higher crosslink density. The first observation that must be noted is that Mc values calculated from DMA results are all lower than those calculated from solvent swell data. As noted from the DSC analysis previously discussed, these coatings are not fully cured (reacted) at room temperature but do undergo substantially more curing when heated. Therefore, the samples characterized via DMA undergo crosslinking during the DMA heating phase, thus increasing crosslink density and lowering Mc. In contrast, the solvent swell samples were cured and analyzed only at room temperature and therefore their crosslink density is understandably lower and their Mc values higher. Nonetheless, it appears that Mc for these coatings stabilizes in the 15,000-25,000 g/mol range after 14 to 21 days. This indicates that SF-1 seemingly has crosslink density sufficient to obtain good solvent and chemical resistance, which agrees with the applied coating properties reported in *Table* 8.

Although cure development of CC-1 and SF-1 with AP-ER was not followed per se, crosslink densities were obtained from applied coatings cured for 21 days at 21°C, 50% relative humidity. *Figure* 5 illustrates an example of these DMA results. The T_g and Mc values of these coatings are reported in *Table* 13 along with results for SF-1 at the same time after application. T_g values are all around 56°C, just slightly above the T_g for SF-1, 46°C. However, crosslink density increases considerably with the substitution of AP-ER, with Mc values decreasing from around 15,000-25,000 to approximately 2300 g/mol. This dramatic increase in crosslink density may be responsible for the improvements in water and scrub resistance when AP-ER is substituted into these systems.

SUMMARY AND CONCLUSIONS

These evaluations confirmed that commercial acrylic-epoxy coatings have long pot life (≥18 hr), short dry times (set-to-touch < 45 min; dry hard < 5 hr), good hardness, moderate chemical resistance, and fairly good weatherability. A range of performance was observed with water resistance, flexibility, and scrub resistance. As a whole, these coatings generally displayed moderate performance relative to industrial coating requirements and high performance relative to architectural applications.

Substitution of AP-ER into these coatings for the specified epoxy component resulted in quicker dry times, higher gloss, better water resistance, and dramatically improved scrub resistance. This modification also holds promise to reduce solvent content of the system due to its ability to film form with lower co-solvent concentrations.

Hardness development of the acrylic epoxy coatings occurred rather slowly and was still improving 30 days after application; however, resistance to MEK double rubs developed in most of the coatings over a four 10-day period. This suggests that ample crosslinking is occurring to impart chemical resistance properties but slow release of volatiles from the coating results in sluggish hardness development. Analysis of film curing via IR spectroscopy indicated little chemical change in the system, including little to no reaction of the epoxy. However, DMA and solvent swell studies indicate crosslink density formation of Mc = 15,000-25,000. Over a 30-day cure at 21°C and 50% RH, T_g values also increase from about 5 to 25°C. DSC analysis of room temperature cured systems confirmed incomplete cure; however, upon a second DSC heating, this exotherm no longer appeared and the system was fully cured. Although room temperature drying did not result in full cure, properties were still good. Substituting AR-EP into the system increased crosslink density of Mc to approximately 2300 g/mol.

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