Epoxy Silanes in Reactive Polymer Emulsions

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Epoxy silanes are effective additives for the crosslinking of carboxy and amino latexes and polyurethane dispersions. A series of epoxy silane additives have been evaluated in both one-pack and two-pack systems. It is found that the structure and water solubility of the epoxy silane as well as the pH of the latex determine silane stability. New water insoluble epoxy silanes achieve long-term shelf stability in emulsions yet crosslink upon application of the coating. Formulating principles, performance improvements, and catalytic cure profiles are reported. Carboxyl-modified waterborne polymer dispersions with post-added epoxy silanes provide curable coatings, in which properties such as mar, chemical and solvent resistance, adhesion, and durability are dramatically improved. In many applications, this approach is a potential candidate for crosslinkable waterborne systems free of aziridines and formaldehyde.

INTRODUCTION

Vinyl and methacrylate hindered-silanes, useful as co-monomers in silylated latexes, have been found effective as low-energy curatives in reactive polymer emulsions as previously described.[1] The aim of this paper is to provide an alternate approach by incorporating silanes directly into the reactive resin formulation as post-additives. In particular, the use of epoxysilane curatives, such as β-(3,4-epoxycyclohexyl)ethyltriethoxysilane (structure 1), β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (structure 2), γ-glycidoxypropyltrimethoxysilane (structure 3), and γ-glycidoxypropylmethyldiethoxysilane (structure 4) is described (see *Figure* 1).

There is a trend in the coatings industry to move to aqueous solution or dispersion type coating compositions due to environmental factors. Much attention has been paid to reactive polymer emulsions because they better provide improved properties such as water and solvent resistance. The availability of reactive functional groups on the latex polymer has allowed the formulator to maximize properties including adhesion and solvent resistance via the post addition of various crosslinkers. At low temperatures, the most widely used crosslinking system has been polyaziridines which crosslink under various drying conditions and are miscible in water and many organic solvents. There are, however, toxicological concerns in using polyaziridines in certain coatings applications. At elevated temperatures, other crosslinking systems are available such as melamines, phenolics, and epoxies. The release of formaldehyde in melamine-containing systems is also a handling concern in some industries.

Certain epoxy silanes have now been found to cure waterborne carboxyl functional latexes and polymer dispersion coatings while avoiding many of these concerns. These epoxy silanes are effective crosslinkers for resins that contain a functional group with an active hydrogen such as carboxylic acid or amine group. These epoxy silanes may be emulsified and their emulsions are easily blended with latexes or dispersion polymers to produce curable systems. Epoxy silanes can be considered as replacements for aziridine, formaldehyde, and melamine systems. A mixture of an epoxy silane emulsion and an acrylic or urethane dispersion polymer can be stable at room temperature for up to a year. Uncatalyzed, these mixtures cure upon heating. They can also function as effective low-energy crosslinkers by incorporating selective catalysts to accelerate the cure. The resulting coatings show improved chemical resistance, adhesion, hardness, and flexibility.

The use of combinations of latex polymers and epoxy resins or compounds is well known.[2] Water-soluble silanes used directly as additives to latex systems have been disclosed in the literature.[3-7] Typical examples of these silanes are epoxy- or aminosilanes, such as γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropylmethyldimethoxysilane, γ-aminopropyltriethoxysilane

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Table 1—Coating Properties of ß-(3,4-epoxycyclohexyl)-ethyltriethoxysilane Emulsion/Carboxyl Acrylic Latex Films vs. the Storage Time of the Admixtures

	Silane Emulsion Concentration (weight %)		
Type of Testing	**0.0%**	**3.0%**	**5.0%**
Gloss (60°):			
0 time	97	87	84
1 week	93	83	76
16 weeks	95	81	gelled
21 weeks	95	79	gelled
Pencil Hardness:			
0 time	3B	HB	F
1 week	4B	B	B
16 weeks	4B	HB	gelled
21 weeks	5B	HB	gelled
MEK Double Rubs:			
0 time	28	>400	>400
1 week	14	>400	>400
16 weeks	9	>400	gelled
21 weeks	10	>400	gelled
Tape Adhesion:			
0 time	5B	5B	5B
1 week	5B	5B	5B
16 weeks	5B	3B	gelled
21 weeks	5B	2B	gelled

SCX™-2500 (from SC Johnson Polymer) was chosen for this study. A 2 wt% of Butyl Proposal® (from Union Carbide Corporation) was added as a coalescing aid. Coatings were prepared on phosphate treated steel panels by a drawdown method. Coatings were baked at 121°C for 20 min and then further cured at 23°C and 50% RH for seven days.

and γ-aminopropyltrimethoxysilane. The employment of emulsified water-insoluble silane additives into latex systems has not been found in the literature. Furthermore, catalytic cure enhancement in relation to epoxy/carboxyl ratio leading to performance improvements has not been reported.

EXPERIMENTAL

Preparation of a 40% β-(3,4-Epoxycyclohexyl)ethyltriethoxysilane Emulsion

Into a beaker was added 3.85 grams of Span® 60 (ICI Americas) and 3.65 grams of Tween® (ICI Americas) which were heated together in a hot water bath in order to melt the solid materials. Sixty grams of β-(3,4-epoxycyclohexyl)ethyltriethoxysilane were added and the mixture was stirred with a mechanical stirrer. Then 82.5 grams of water were added and the mixture was stirred vigorously for approximately five minutes to provide a white emulsion containing 40% by weight of epoxy functional silane.

Table 2—The MEK Resistance of Films Cast from Carboxylated Acrylic Latexes Containing 2% of Emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (A), octyltriethoxysilane (B), 1-triethoxysilyl-2-methyldiethoxysilylethane (C) and amyltriethoxysilane (D). The Latexes with no Additive were Conducted as a Control (E)

	MEK Double Rubs (times)				
	Sample Code				
Type of Latex	**A**	**B**	**C**	**D**	**E**
Latex 1	130	14	13	8	8
Latex 2	182	11	9	9	8

During formulating, dipropylene glycol (1% of weight) or Dowanol DB (2% of weight) was added to the carboxylated acrylic latex. Latexes 1 and 2: Joncryl® 77 and 95 from SC Johnson Polymer. Coatings were prepared on phosphate treated steel panels by a drawdown method. Coatings were baked at 121°C for 20 min then cured at 23°C and 50% RH for seven days.

Preparation of a 40% γ-Glycidoxypropylmethyldiethoxysilane Emulsion

Into a beaker was added 1.93 grams of Span 60 and 2.87 grams of Myrj® 52S (ICI Americas) which were mixed and heated together in a hot water bath in order to melt the solid materials. Twenty-four grams of γ-glycidoxypropylmethyldiethoxysilane were added and the mixture was stirred with a mechanical stirrer. Next, 31.2 grams of water were added and the mixture was stirred for approximately 30 min to provide a white emulsion containing 40% by weight of epoxy functional silane.

Preparation of Epoxysilane/Reactive Emulsion Polymer Admixtures

Admixtures are prepared by adding various amounts of epoxysilane emulsions or water soluble epoxysilanes into reactive emulsion polymers which contain active hydrogen bearing groups. For example, admixtures of carboxyl functional latexes containing 2% by weight of emulsified silane were prepared by adding 5.26 g of 40% β-(3,4-epoxycyclohexyl)ethyltriethoxysilane emulsion to 100 g of the latexes.

Testing Methods

Coatings were prepared from these admixtures using a draw down method. Coatings were baked at 121°C for 20 min and/or cured at 23°C and 50% RH for seven days. The dry film thickness was two mils. MEK resistance of the coatings was conducted according to ASTM D 4752. The values reported are number of double rubs required to expose the substrate and were determined by averag-

Table 3—The Viscosity and pH Values of Carboxylated Acrylic Latexes Admixed with Various Concentrations of a ß-3,4-epoxycyclohexyl)ethyltriethoxysilane Emulsion over the Periods of Storage at RT

	Silane Emulsion Concentration (weight %)			
Type of Testing	**0%**	**0.5%**	**1.0%**	**5%**
Viscosity (cps)				
0 time	28	50	65	148
1 week	30	49	62	146
2 weeks	29	50	64	107
6 months	45	63	75	gelled
pH				
0 time	8.5	8.5	8.5	8.6
1 week	8.5	8.6	8.6	8.9
2 weeks	8.4	8.5	8.6	9.1
6 months	7.9	8.1	8.3	gelled

SCX 2500 was chosen for this study. During the formulation, 1% of dipropylene glycol was added as a coalescent agent.

ing three tests done on the same steel panels. Gloss values were performed according to ASTM D 523.

Pencil hardness was performed according to ASTM D 3363. The crosscut tape adhesion test was performed according to ASTM D 3359. The wet adhesion between a film from the dispersion coated on a substrate and the substrate was measured according to Method 6301 of U.S. Federal Standard Test Method 141B.

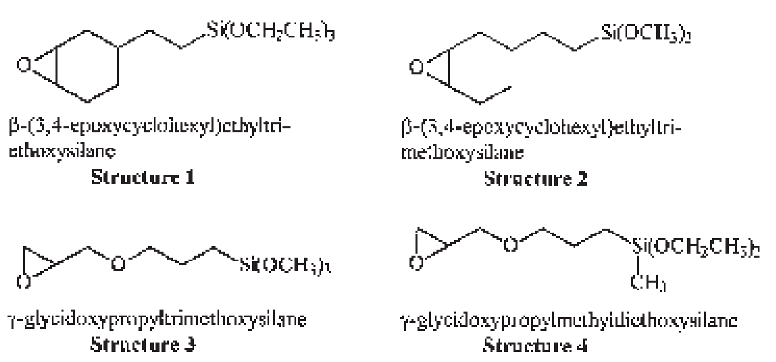

Figure 1—Structures of epoxy silanes.

RESULTS AND DISCUSSION

The Role of Epoxysilane Curing in Performance Improvement

The mixture of a reactive latex and an epoxysilane additive forms an aqueous polymer system for crosslinks on drying under ambient conditions or at elevated temperatures to form a crosslinked film or finish. Films cast from the carboxylic latex-epoxysilane admixtures show improved properties, such as solvent resistance, adhesion, hardness, and mar resistance, compared to controls with no additives.

Epoxysilane emulsion additives impart a smooth coating surface. Coatings containing neat water insoluble epoxysilane additives sometimes form surface defects, such as craters or gel particles. Alternatively, these silanes can be pre-dissolved in solvent and blended into the system instead of being pre-emulsified by surfactants. Thus, the relatively water-insoluble epoxysilanes, such as β-(3,4-epoxycyclohexyl)ethyltriethoxysilane, best serve as crosslinkers when emulsified, or dispersed in solvent or systems containing surfactants. Glycidoxy silanes are more reactive than the epoxycyclohexyl silanes, and therefore are best used as additives in ambient cure two pack systems.

The coating properties of films cast from an acrylic latex with an acid number of 19 containing different concentrations of β-(3,4-epoxycyclohexyl)-ethyltriethoxysilane emulsion are described in *Table* 1. A control experiment without silane emulsion was conducted for comparison. The results showed that the MEK resistance and pencil hardness of the coatings was improved by the addition of epoxysilane emulsion.

The mechanism of crosslinking involves the epoxysilane's dual chemical functionality. The epoxy portion of the molecule is reactive with the matrix resin's carboxylic groups and the alkoxysilane portion crosslinks with another silane molecule after hydrolysis, by condensation forming siloxane bonds. The alkoxysilanes also can react with surfaces to improve wet adhesion of the coating, or with fillers to improve pigment binding.

When incorporating epoxysilanes directly into the resin formulation, their stability in the emulsion lies in factors such as silane structure and solubility and pH of the system. The majority of trialkoxysilanes do not become soluble until the alkoxy groups hydrolyze. Hydrolysis of the alkoxy groups requires molecular contact of water with the alkoxysilane. Premature hydrolysis of the silane can cause premature crosslinking of the latex. These epoxysilane emulsions are colloidally stable in water avoiding the problem of premature hydrolysis, yet will hydrolyze and condense (crosslink) upon coalescing into a film and exposure to a catalyst or heat.

Epoxycyclohexyl silanes (structures 1 and 2) are more stable in aqueous systems than the glycidoxy silanes (structures 3 and 4) due to their greater hydrophobicity and non-terminal epoxy moiety. The hydrolysis rate of trimethoxy silanes is generally slower than trimethoxy silanes adding to the water stability of this silane.

The MEK resistance of films cast from carboxylated acrylic latexes containing emulsified epoxysilanes and nonfunctional alkoxysilanes is described in *Table* 2. A control without silane emulsion was included for comparison (E). The results clearly demonstrate the role of the epoxy functionality in improving the solvent resistance of the coatings. The subsequent siloxane crosslinking formation apparently involves the reaction of the carboxyl group of the latex and the epoxy group of the silane

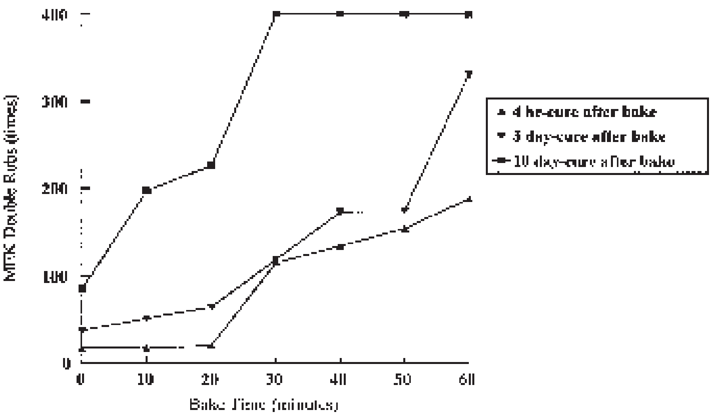

Figure 2—MEK resistance of carboxylated acrylic latex coatings with 3% emulsified β-3,4-epoxycyclohexyl)-ethyltriethoxysilane vs. bake time at 66°C.

Table 4—The MEK Resistance of Films Cast from a Carboxylated Acrylic Latex (A) and the Latex Containing 2% of Emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (B), neat ß-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (C), neat γ-glycidoxypropyltrimethoxysilane (D), neat γ-glycidoxypropylmethyldiethoxysilane (E), emulsified-3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (F), neat 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (G), neat ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (H)

	MEK Double Rub (times)							
	Sample Code							
Cure Condition	A	B	C	D	E	F	G	H
Cured at 121°C	11	130	169	171	127	9	45	34
Cureda at 23°C	14	41	41	110	87	8	—	—

During formulation, dipropylene glycol (1% of weight) was added to the latex, Joncryl 77. Coatings were prepared on phosphate treated steel panels by a drawdown method. 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate is from Union Carbide.

—: Test was not conducted.

Table 5—The MEK Resistance of Films Cast from a Carboxylated Acrylic Latex (A), and the Latex Containing 2% of Emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (B), neat ß-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (C), neat γ-glycidoxypropyltrimethoxysilane (D), neat γ-glycidoxypropylmethyldiethoxysilane (E), emulsified 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (F), neat 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (G), neat ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (H)

	MEK Double Rub (times)							
	Sample Code							
Cure Condition	A	B	C	D	E	F	G	H
Cured at 121°C	7	182	22	241	21	22	46	51
Cured at 23°C	8	19	—[a]	57	—[a]	12	—	—

During formulation, dipropylene glycol (1% of weight) was added to the latex, Joncryl 95. Coatings were prepared on phosphate treated steel panels by a drawdown method.

(a) Surface defects with craters resulted on the coating. —: Test was not conducted.

(A). Those silanes with no ability to bond to the resin offered no improvement in MEK rubs (B, C, and D).

A vinyl acrylic latex was prepared with the co-monomers vinyl acetate and butyl acrylate at a weight ratio of 85/15 by a semi-continuous batch process. The non-carboxylic vinyl acrylic latex was used as a model to demonstrate the role of carboxyl functionality to effect the solvent resistance of coating films, when using epoxysilane emulsions as additives. The MEK resistance of films cast from the admixture containing 10% of the emulsified epoxysilane is reported as 15 double rubs. The control vinyl acrylic latex without silane additive is five double rubs. Therefore, little or no improvement in the solvent resistance of the non-carboxylic vinyl acrylic films was found, even at a 10% emulsified epoxysilane additive concentration. The results clearly demonstrate the important role of carboxyl functionality to effect the solvent resistance of coating films, when using epoxysilane emulsions as additives. Siloxane crosslinking is ineffective in improving properties of the coating if the silane is not chemically bound to the latex polymer.

Table 6—Coating Properties of Films Cast from a Carboxylated Acrylic Latex Containing 2% Silanes. The Silanes in the Acrylic Emulsions are Emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (A), emulsified γ-glycidoxypropylmethyldiethoxysilane (B), neat γ-glycidoxypropyltrimethoxysilane (C), and emulsified 3,4-epoxycyclohexylmethyl-3,4-epoxyclohexylcarboxylate (D). A Coating from the Latex with No Additive (E) was Tested as a Control

	Sample Code				
Test Method	A	B	C	D	E
Gloss value					
20°	84	78	64	80	89
60°	97	99	92	99	105
Pencil hardness	HB	H	F	B	B
Tape adhesion	5B	5B	5B	5B	5B
Wet adhesion	10	10	10	10	10

Dowanol DB (from Dow Chemical) was added 2% by weight as a coalescing aid.

Stable One-Pack Epoxycyclohexylsilane Emulsion/Reactive Latex System

When properly emulsified this epoxy silane remains as an unhydrolyzed monomer during storage so it has maximum effectiveness as an adhesion promoter when the latex is applied to a surface and dried. Forty percent β-(3,4-epoxycyclohexyl)ethyltriethoxysilane emulsion has a shelf stability of more than a year. The admixtures of carboxylated acrylic latexes with emulsified β-(3,4-epoxycyclohexyl)ethyltriethoxysilane generally afford stable dispersions at room temperature for at least six months. Since silane hydrolysis is effected by pH, one-pack coating systems are best formulated between pH 6 and 8.

The long-term formulation stability of a one-pack system was determined by viscosity and visual inspection of the degree of particle sedimentation or

Table 7—Coating Properties of an Acrylic Latex With and Without Epoxysilane Additives

	Molar Ratio of Epoxy to Carboxyl Functionality			
Type of Epoxysilane	**No Silane**	**0.27/1.0**	**0.75/1.0**	**1.0/1.0**
7 days at RT-γ-glycidoxypropyltrimethoxysilane:				
MEK double rubs (times)	28	50	146	>400
ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane emulsion:				
MEK double rubs (times)	—	50	>400	346
Mar resistance:				
Thumb nail	Scratch	No scratch	No scratch	No scratch
Flexibility	Brittle	Brittle	Flexible	Flexible
Pencil hardness	H	2H	H	H
After 10 min flash, 10 min @ 120°F and 7 days RT cure-γ-glycidoxypropyltrimethoxysilane:				
MEK double rubs (times)	28	>400	>400	>400
ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane emulsion:				
MEK double rubs (times)	—	75	117	>400

Epoxysilanes were added to an acrylic latex, Rhoplex® CL-105 (from Rohm and Haas), formulation WR-55-2. The pH of the admixtures was 7.3. Coatings were prepared on aluminum panels by drawdown method, allowed to cure at RT for seven days.

gelation in the dispersion. Emulsified β-(3,4-epoxycyclohexyl)ethyl-triethoxysilane was mixed with a carboxylated acrylic latex to give final silane concentrations of 0.5%, 1.0% and 5.0% by weight. The viscosity and pH values of these admixtures monitored over the period of storage at RT are presented in *Table* 3. The values of pH and viscosity went up slightly for the admixture containing five percent by weight of epoxysilane after two weeks and this mixture gelled after six months. The gelation is likely due to the instability of the silane emulsion in this higher pH range. The admixtures maintained constant viscosity and pH values at room temperature for a period of at least six months at 0.5% and 1.0% by weight of epoxysilane emulsion. The coatings performance also maintained when viscosity was constant during storage (see *Table* 1).

Glycidoxy Silanes for Two-Pack Systems

Glycidoxy silanes are more reactive than epoxycyclohexyl silanes limiting their use to two-pack systems. When the admixtures of epoxysilanes and carboxyl latexes were freshly made, relatively water soluble neat γ-glycidoxypropyltrimethoxysilane additive gave comparable solvent resistance to less water soluble neat β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and the emulsified β-(3,4-epoxycyclohexyl)ethyltriethoxysilane additives. However, latexes containing two to five percent γ-glycidoxypropyltrimethoxysilane gelled within days. Also, a 40% γ-glycidoxypropylmethyldiethoxysilane stock emulsion was stable only for several days.

The crosslinking ability of various epoxysilane additives in a self-curing aqueous emulsion binder system was examined for two-pack systems. Coating performance was compared among carboxylated latexes with these curing agents and described in *Tables* 4-6. A commercial epoxy resin, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate was studied as a reference sample. The cure conditions include room temperature and elevated temperature (121°C for 20 min) and then cured at room temperature (23°C) and 50% RH for seven days.

The results show that γ-glycidoxypropyltrimethoxysilane cures faster than other epoxysilane

Table 8—Cure Profile at RT at Carboxylated Acrylic Latex Coatings With and Without 3% Emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane

	RT Cure Time			
Type of Testing	**4 Hr**	**3 Days**	**7 Days**	**10 Days**
Without additive:				
Pencil hardness	<5B	2B	2B	2B
MEK double rubs	18	8	21	7
With silane emulsion:				
Pencil hardness	<5B	5B	3B	3B
MEK double rubs	17	37	74	85

A 2 wt% of 2-(2-butoxyethoxy)ethanol was added as a coalescing aid. Coatings were prepared on aluminum panels by a drawdown method. SCX 2500 was chosen as a model latex system. Coatings were cured at RT and tested at 4 hr, 3, 7, and 10 days.

Table 9—Cure Profile at RT at Carboxylated Acrylic Latex Coatings With and Without 3% Emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane Additive after Baking at 116°C for 10 Min

	RT Cure Time After Bake			
Type of Testing	**4 Hr**	**3 Days**	**7 Days**	**10 Days**
Without additive:				
Pencil hardness	2B	2B	2B	F
MEK double rubs	19	19	17	10
With silane emulsion:				
Pencil hardness	2B	2B	H	HB
MEK double rubs	>400	>400	>400	>400

A 2 wt% of 2-(2-butoxyethoxy)ethanol was added as a coalescing aid. Coatings were prepared on aluminum panels by a drawdown method. SCX 2500 was chosen as a model latex system. Coatings were cured at RT and tested at 4 hr, 3, 7, and 10 days.

Table 10—Coating Property Improvement of an Acrylic Latex With and Without the Addition of ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane and Various Catalysts

	RT Cure Time After Bake		
Type of Testing	4 Hr	3 Days	7 Days
Control without additive:			
Pencil hardness	2B	B	2B
MEK double rubs	19	17	19
With 3% silane emulsion:			
Pencil hardness	B	B	B
MEK double rubs	33	30	149
With 3% silane emulsion and 1% EMI-24[a]:			
Pencil hardness	B	B	B
MEK double rubs	21	219	>400
With 3% silane emulsion and 1% 1-(2-(trimethylsily)propyl)-1H-imidazole:			
Pencil hardness	2B	B	F
MEK resistance	72	219	>400
With 3% silane emulsion and 1% N,N-dimethylbenylamine[b]:			
Pencil hardness	B	HB	HB
MEK resistance	26	68	192

(a) Imicure EMI-24 curing agent is from Air Products and Chemicals.
(b) N,N-Dimethylbenylamine is from Zeeland Chemicals, Inc.
Phoplex CL-204 was used, Coatings were prepared on phosphate treated steel panels by a drawdown method.

additives. However, the comparative neat β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and γ-glycidoxypropylmethyldiethoxysilane gave sporadic surface defects. The system containing the emulsified β-(3,4-epoxycyclohexyl)ethyltriethoxysilane additive showed no such surface defects. The emulsified 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate additive provided little or no improvement in solvent resistance to the dried latex film.

Formulation Principles

Solubility and pH control the stability of the epoxy silanes in an aqueous environment. Thus, relatively water insoluble epoxy silanes achieve long-term shelf stability in emulsions. It is found that the achievement of desirable properties depends on the acid number, epoxy/carboxyl ratio and cure conditions. High acid functionality latexes with stoichiometric equivalent epoxysilane amounts of curing agents result in high crosslink density.

Factors controlling the initial hardness/print resistance include the T_g of the film, amount of epoxy silane and the coalescing aid. For ambient cure applications, selection of high print resistance carboxylated latexes for use with epoxysilane curing agents helps achieve superior ultimate properties such as mar, solvent, and chemical resistance.

The epoxysilane additives are compatible with many latex systems. For clear coatings such as wood topcoats, the compatibility of additives with the latex is a critical issue since clarity of the final coating is important. Careful choice in the formulation of epoxysilane emulsions, such as surfactant, co-solvent and pH, will avoid haziness or incompatibility. Emulsification of epoxysilanes may not be needed if the coating formulation has abundant surfactants or co-solvent contact. The low viscosity of the waterborne epoxy silanes allows the formulator and compounder to use them easily in waterborne systems. Additionally, the VOCs of a formulation may be reduced by the addition of epoxysilanes, since these silanes may act as reactive diluents to decrease the minimum film forming temperature (MFT) while maintaining performance of the cured film.

Table 11—The Coating Properties of Film Cast from an Emulsion of Urethane-Acrylic Hybrid Polymer With and Without the Addition of γ-glycidoxypropyltrimethoxysilane (A) and emulsified ß-(3,4-epoxycyclohexyl)ethyltriethoxysilane (B)

	Epoxysilane Additives (%)			
Type of Testing	0%	3% A	5% A	3% B
Room temperature cure for 7 days:				
Pencil hardness	H	H	2H	H
i-Propanol rubs[a]	200	280	>400	250
After baking @ 121°C for 20 min and room temperature cure for 7 days:				
Pencil hardness	H	H	H	F
i-Propanol rubs[a]	260	>1300	>1300	370

(a) The i-propanol resistance was determined by the double rub numbers of a cheesecloth-wrapped hammer saturated with i-propanol, rubbing to expose the aluminum panel. Flexthane 620 from Air Products was used. Coatings were prepared on aluminum panels by a drawdown method.

Wood Coating Applications

The solvent resistance of a wood coating acrylic latex, crosslinked with β-(3,4-epoxycyclohexyl)ethyltriethoxysilane and γ-glycidoxypropyltrimethoxysilane is described in *Table* 7 using two different cure cycles. The epoxy/carboxyl ratio was varied between 0.27/1.0 and 1.0/1.0. The MEK double rub numbers increase as the epoxy/carboxyl ratio reaches unity. Flexibility and mar resistance are also improved by epoxysilanes.

Time-Temperature Cure Profile

In the absence of a catalyst, the cure profile of carboxylated acrylic latex coatings with and without the addition of emulsified β-(3,4-epoxycyclohexyl) ethyltriethoxysilane additive was studied by pencil hardness and MEK resistance from room temperature to 116°C. *Tables* 8 and 9 list the performance of coatings cured at room temperature and 116°C (10 minutes). The cure behavior is shown versus the cure time of four hours, three, seven, and 10 days. The carboxyl/epoxy reaction is heat activated. The MEK resistance of these epoxysilane/carboxylated latex films cured at four hours, three days and 10 days was further plotted versus bake cycles at 66°C. (See *Figure* 2).

Catalytic Effects on the Cure Behavior

Low-energy cure can be accelerated by incorporating catalysts in the systems. Selective catalysts have been found further promoting cure reactions and thus enhancing the performance.

Table 10 demonstrates the superior low temperature cure obtained when a catalyst is present in the composition. A carboxylated latex was studied. Coatings were baked at 66°C for 15 min. The coating properties of the cured product at room temperature were determined after four hours, three days, and seven days. Development of MEK resistance at lower temperature and shorter time was greatly enhanced by these catalysts.

Improvement of Solvent Resistance in Polyurethane Dispersions

Epoxysilane additives enhance the solvent resistance in films prepared from carboxyl urethane dispersions. Coating films prepared from an emulsion of urethane-acrylic hybrid polymer for use in high performance wood, plastic, and industrial coatings and overprints with epoxysilane additives have been studied on aluminum panels. Significant improvement in isopropyl alcohol resistance is reported in *Table* 11.

CONCLUSIONS

Epoxysilane curing agents function as low energy crosslinkers and adhesion promoters. They are reactive with hydrogen-active polymer emulsions, such as carboxylated acrylates. They have been found to improve solvent, alcohol, and water resistance, to increase hardness, and to improve adhesion in many commercial latexes and polyurethane dispersions.

Cycloaliphatic epoxysilane emulsion additives in water based dispersion polymer systems afford stable one-pack aqueous emulsions without formation of gel particles. Glycidoxy silanes serve as additives in two-pack systems for rapid and effective cure. The cure reactions are accelerated by selective catalysts for low-heat applications. Carboxyl-modified waterborne polymer dispersions with post-added epoxy silanes provide curable compositions suitable for use in wood and industrial coatings, architectural paints, adhesives, and sealants and textiles.

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