

# Novel Ambient Temperature Curable Two-Component Waterborne Silicone-Acrylic Coatings

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## INTRODUCTION

Environmentally friendly coatings have been developed to meet VOC regulations around the world.<sup>1-3</sup> There is also strong demand to develop an isocyanate-free and ecologically safe coating system that provides excellent film properties similar to those of two-component (2K) ambient-cure acrylic urethane systems.<sup>4-6</sup>

An ambient curable waterborne (WB) coating is one of the candidates for such demands. However, WB coatings generally are composed of resins containing hydrophilic functional groups (e.g., neutralized carboxylic acid groups, polyethylene oxide groups, etc.). These groups usually remain in the final coating film and can have a negative effect on film properties such as weatherability and resistance to water and alkali. Therefore, it is generally believed that WB coatings cannot provide the excellent film properties of conventional organic solvent types.

One approach is to reduce the content of hydrophilic groups in the resin to the minimum for preparation of the WB resin so that the concentration of functional groups remaining in the film can be reduced. Such an approach however, is not likely to result in excellent film properties.

There are other approaches<sup>7-9</sup> for ambient curable WB coatings, however, they are expected to have some drawbacks on the film properties. For instance, a film made from a one-component waterborne silicone-acrylic resin system has poor solvent resistance. In this system the self-condensation of alkoxy silyl groups can occur in the dispersing particles in water but insufficient inter-particle crosslinking occurs after formation of the film.

The 2K WB acrylic-urethane system provides a cured film having poor water resistance caused by the remaining hydrophilic groups and unreacted hydroxyl groups. The 2K WB epoxy curing system also provides a film having poor water resistance caused by the remaining hydrophilic groups in a poly-epoxy hardener or the unreacted functional groups.

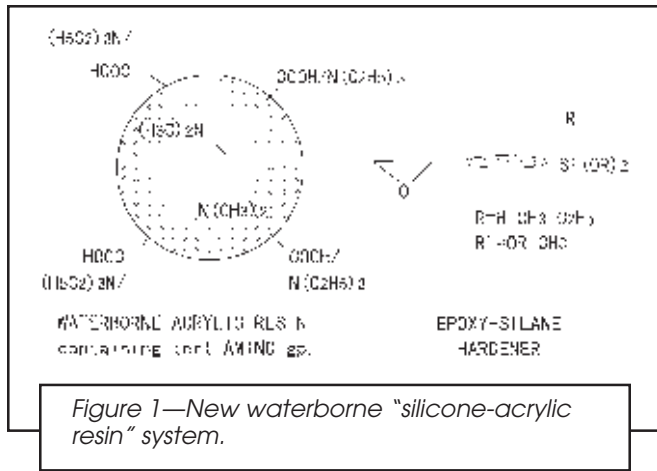
*Waterborne coatings are composed of resins containing hydrophilic functional groups. These groups usually remain in the coating film and can adversely affect film properties such as weatherability and resistance to water and alkali. We have developed a novel ambient temperature curable waterborne two-component system, in which the hydrophilic functional groups are consumed by the crosslinking reaction. The new coating system consists of a waterborne acrylic resin containing both tert-amino and carboxylic acid groups and a hardener containing both epoxy and alkoxy silyl groups. The waterborne silicone acrylic coatings provide superior film properties even if the acrylic resin has relatively low functional group content.*

*In this paper we describe the crosslinking reaction mechanism and film properties using some acrylic resin types and paint formulations as examples.*

We have studied the isocyanate-free and ambient temperature curable WB 2K coating system, in which hydrophilic functional groups can be consumed by the crosslinking reaction and which can overcome the defects of the conventional WB system.

The system studied consists of a waterborne acrylic polymer containing carboxylic acid groups neutralized with a tert-amino compound, and an epoxy-silane compound (e.g.,  $\gamma$ -glycidoxypropyltrimethoxysilane ( $\gamma$ -GPTMS)) as the hardener (see Figure 1).

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In this system, since the hardener is mixed with the waterborne acrylic polymer just prior to use and the mixture used before the condensation of silyl group is complete, the system can provide sufficient curability.

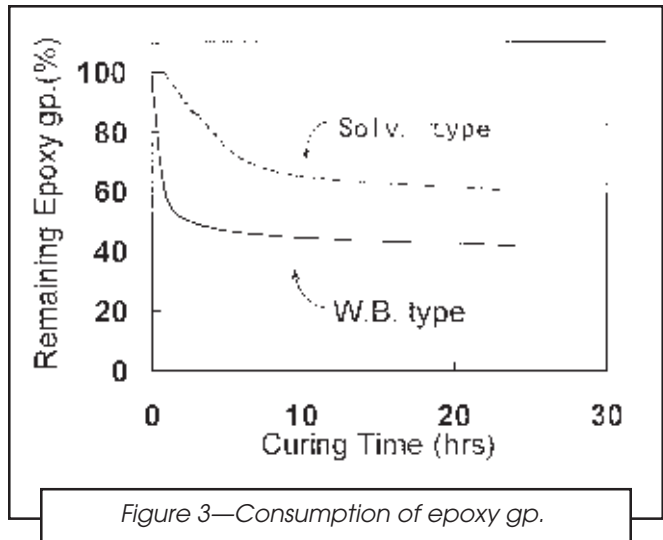
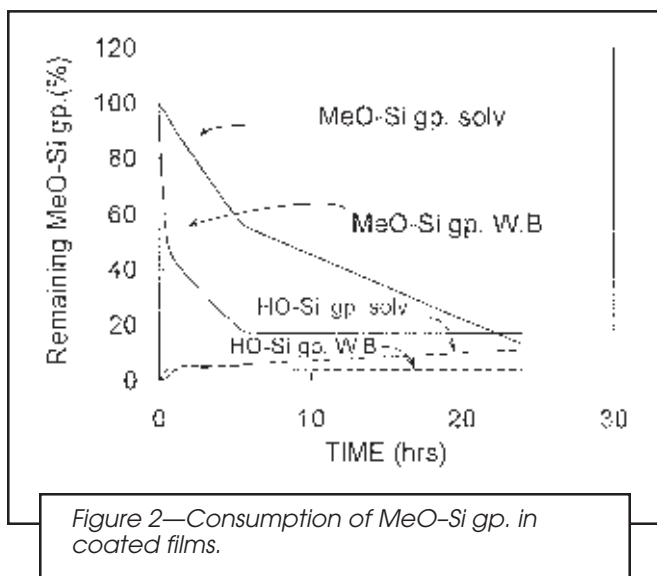
Curing takes place via three reactions:

- (1) the reaction between the tert-amino groups of the WB resin and the epoxy groups of the hardener;
- (2) the reaction between the carboxylic acid groups of the WB resin and the epoxy; and
- (3) the condensation reaction of the silyl groups.

In this paper we describe the crosslinking reaction mechanism of the system, the typical film properties of this crosslinking system, and the distribution of Si atoms in the film.

## EXPERIMENTAL MATERIALS

**Model A of Acrylic Resin Solution Type:** Styrene-(meth)acrylate co-polymer containing 3.3 wt% of dimethylamino-ethylmethacrylate (DM) and 3 wt% of acrylic acid (AA) (on total monomers) in methyl ethyl ketone (MEK), non-volatile content (=60 wt%, viscosity =



$U^2 - V$  (Gardner 25°C). This acrylic resin solution was diluted to 30% (NV) by organic solvents (xylene/butylacetate = 70/30 wt%).

**Model B of WB Resin Type:** The same acrylic resin described previously was neutralized with triethylamine (TEA) so that the molar ratio of TEA to AA was 1:1. Water was added to the neutralized resin to form WB resin (Dispersion: NV = 30%).

**Model C of Acrylic Resin Solution Type (used only for FTIR analysis):** Styrene-(meth)acrylate co-polymer containing 5 wt% of DM and 10 wt% of acrylic acid (AA) (on total monomers) in MEK, non-volatile content (NV = 57.7 wt%, viscosity =  $Z_6^2 - Z_7$  (Gardner 25°C). This acrylic resin solution was diluted to 30% (NV) by organic solvents (xylene/butylacetate = 70/30 wt%).

**Model D of WB (used only for FTIR analysis):** The same acrylic resin described earlier was neutralized with TEA so that the molar ratio of TEA to AA was 1:1. Water was added to the neutralized resin to form WB resin (NV = 30%).

Table 1—Reactivity of Varied Epoxy-Silane Hardeners

Epoxy-Silane Hardener	Gol-fraction %	MEK rubbing
Gly-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -Si(OEt) <sub>3</sub>	95	Excellent
Gly-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -Si(OEt) <sub>2</sub> Cl	90	Good
$\begin{array}{c} \text{OCH}_3 \\   \\ \text{O-Si} \\   \\ \text{Cl} \end{array} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{Gly}$	88	Poor
$\begin{array}{c} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{Gly} \\   \\ \text{---} \text{O-Si} \text{---} \\   \\ \text{CH}_3 \end{array}$	87	Poor

Gly: Glycidyl group

Table 2—Paint Formulations

WB Silicone Acrylic Resin	Acrylic-Urethane (Solvent Type)	Conventional Acrylic Emulsion
Amino/carboxylic acid ..... functional acrylic polymer <sup>a</sup> ..... 40.74	Acrylic polymer <sup>a</sup> ..... 32.87	Styrene acrylic emulsion polymer <sup>a</sup> ..... 57.9
TEA ..... 1.17	TiO <sub>2</sub> <sup>h</sup> ..... 18	Deionized water ..... 7.76
Deionized water ..... 34.77	Thinner ..... 35.04 (Xylene/butylacetate=70/30)	10% sodium tripolyphosphate ..... 0.5
TiO <sub>2</sub> <sup>h</sup> ..... 19.11	Polyisocyanate resin <sup>f</sup> ..... 14.09	Polyoxyethylenonyl- ..... 0.24 phenylether (HLB=12)
Epoxy silane hardener <sup>b</sup> ..... 4.21	Total ..... 100	28% aq. NH <sub>4</sub> OH ..... 0.05
Total ..... 100		Ethyleneglycol ..... 1.92
		TiO <sub>2</sub> <sup>h</sup> ..... 26.63
		2,2,4-trimethyl-1,3-pentanediol monoisobutyrate ..... 5
		Total ..... 100
<b>Solv. Silicone Acrylic Resin</b>		
Amino-functional acrylic polymer <sup>c</sup> .. 43.57		
TiO <sub>2</sub> <sup>h</sup> ..... 17.28		
Thinner ..... 31.75 (Xylene/butanol=70/30)		
Epoxy silane hardener <sup>d</sup> ..... 7.4		
Total ..... 100		

(a) Watersol YW-559: Product of Dainippon Ink and Chemicals Inc.; acrylic polymer containing tert-amino groups and carboxylic-acid, non-volatile content=59-61%. Solvent=propyleneglycol mono-iso-propylether  
 (b) Watersol WW-565: Product of Dainippon Ink and Chemicals Inc.; hardener containing an epoxy-silane.  
 (c) Acrylic A-9510: Product of Dainippon Ink and Chemicals Inc.; acrylic polymer containing tert-amino groups. Non volatile content=49-51%. Solvent=toluene and iso-butanol.  
 (d) Acrylic A-9585: Product of Dainippon Ink and Chemicals Inc.; hardener containing an epoxy-silane. Effective solid content=80%.  
 (e) Acrylic A-801-P: Product of Dainippon Ink and Chemicals Inc.; acrylic polymer. OHV=47-53. Non-volatile content=49-51%. Solvent=toluene and ethylacetate).  
 (f) Burnock DN-950: Product of Dainippon Ink and Chemicals Inc.; polyisocyanate resins. NCO content=12-13%. Non-volatile=74-76%. Solvent=ethylacetate).  
 (g) Voncoat EC-889: Product of Dainippon Ink and Chemicals Inc.; styrene-acrylic emulsion polymer. Non-volatile content=49-51%. Viscosity=200-1500cps. pH=8.0-10.0. MFT(°=28).  
 (h) Tipaque R-930: Product of Ishihara Sangyo Kaisha Ltd., rutile titanium dioxide, 93% assay. Meets ASTM D 476, type IV. Specific gravity=4.2.

**Model Hardener:**  $\gamma$ -Glycidoxypropyl trimethoxysilane ( $\gamma$ -GPTMS,  $\gamma$ -Methacryoxypropyltrimethoxysilane ( $\gamma$ -MPTMS),  $\gamma$ -Glycidoxypropyl-methyldimethoxysilane,  $\gamma$ -Methacryloxypropylmethyldiethoxysilane, and the other silicone compounds listed in Table 3 (produced by Nippon Unicar Co. Ltd. and Toray Dow Corning Silicone Co., Ltd.) were used without any further purification.

## RESULTS AND DISCUSSION

We studied the crosslinking reactions using model compounds. What we tried to elucidate are the reaction on silyl and epoxy groups of the hardener and the influences of water and amine neutralizer on curing. While many studies have been done to elucidate the reactivity of alkoxysilane compounds,<sup>10</sup> there are few studies of the reactivity of the silyl group in polymers or coating films.<sup>11-14</sup>

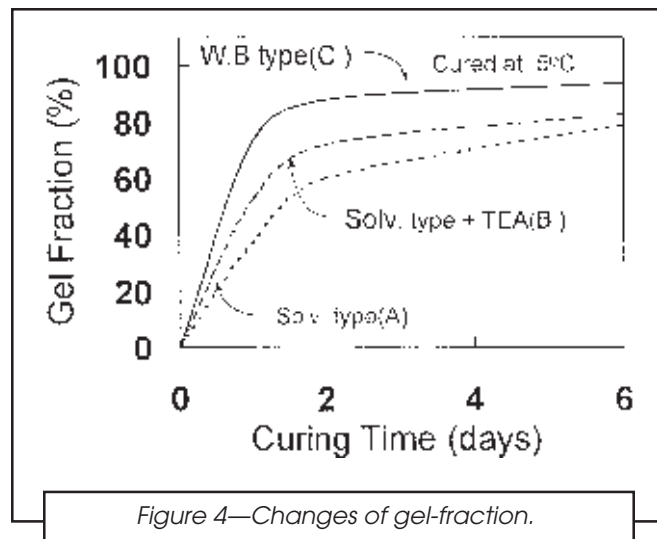
### Crosslinking Mechanism

To determine the kinetics of the self-condensation reaction of the silyl groups in the films made from the waterborne silicone acrylic resin system and to take the influence of functional groups in the polymers into consideration (1) Model A +  $\gamma$ -MPTMS and (2) Model B +  $\gamma$ -MPTMS were employed. In this case,  $\gamma$ -MPTMS was selected to replace  $\gamma$ -GPTMS which generates OH functionality from the epoxy-carboxylic acid addition and complicates the determination. The mixtures were coated on the KBr plate and KRS plate, respectively. The absorption intensity changes of the functional groups were measured by FTIR (Si-OH: 3400-3450 cm<sup>-1</sup>; Si-OCH<sub>3</sub>: 820 cm<sup>-1</sup>). The Si-OH group was determined using a calibra-

tion curve which had been prepared previously by the relationship between the varied Si-OH group content of diphenyldisilanol in  $\gamma$ -MPTMS and the corresponding intensity of the absorption. The results are plotted in Figure 2.

More than 80% of the -Si-OCH<sub>3</sub> group was hydrolyzed within six hours in the WB system, and approximately five percent of -Si-OH group (based on the corresponding initial -Si-OCH<sub>3</sub> group as 100%) was detected constantly during the cure reaction. The condensation reactions are faster in the WB system than those in the corresponding organic solvent type due to the influence of the water medium.

Next, for the easier determination of epoxy groups by IR spectra, Models C and D, which have more functional



**Table 3—Film Properties**

	WB Silicone Acrylic Resins	Solv. Silicone Acrylic Resin	Acrylic-Urethane (solvent type)	Convention Acrylic Emulsion
Gloss 20 .....	78	79	85	26
60 .....	89	89	92	74
Pencil hardness .....	F	H	F-H	<6B
Gel fraction % .....	95	94	91	77
MEK rubbing 1.5kg/100 times .....	Excellent	Good	Excellent	Poor
Alkali resistance 5% NaOH r.t. 24 hr .....	Excellent	Excellent	Excellent	Excellent
Acid resistance 5% H2SO4 r.t. 24 hr .....	Excellent	Blister 6D	Excellent	Excellent
Impact resistance cm .....	50<	30-35	50<	50<
(DuPont 1/2", 500 g)				
Water resistance .....	Excellent	Excellent	Excellent	Poor
(immerse in water r.t. 7 days)				
<b>Adhesion</b>				
Steel .....	100%	100%	100%	100%
after the test .....	100%	100%	100%	0%
(blister box 50°C R.H.-98%, 24 hr)				
Aluminum .....	100%	100%	0%	50%
after the test .....	100%	100%	0%	90%
Chrome plate .....	100%	100%	60%	100%
after the test .....	100%	100%	60%	0%
Stainless steel .....	100%	100%	100%	100%
after the test .....	100%	100%	100%	0%
Slate .....	100%	100%	90%	90%
after the test .....	80%	90%	80%	0%
(immerse in water r.t. 7 days)				

Curing condition: r.t. for 7 days.

groups than the actual film forming resins (e.g., the model B resin), and the corresponding amount of  $\gamma$ -GPTMS were used. The consumption of the epoxy group is also faster in the WB system than in the corresponding organic solvent type as shown in Figure 3.

Figure 4 shows the changes with time of the gel-fraction in the cured films made from the acrylic polymers and the hardener:

- (a) Composition A: Model A (containing tert-amino group and carboxylic acid group) and  $\gamma$ -GPTMS.
- (b) Composition B: Model A neutralized with TEA in the organic solvent and  $\gamma$ -GPTMS.
- (c) Composition C: Model B (the neutralized A in water) and  $\gamma$ -GPTMS.

The comparison of the changes in gel-fraction among the three compositions shows that TEA acts as a catalyst for the crosslinking reaction; and water also can accelerate the crosslinking reaction.

Stress-strain testing of cured films formed from water-borne silicone acrylic systems with AA content 2% and 4% was carried out to examine the contribution of the carboxylic acid group to the crosslinking reaction. The stress-strain curve (Figure 5) shows that the tensile strength increases with the content of the carboxylic acid group. In

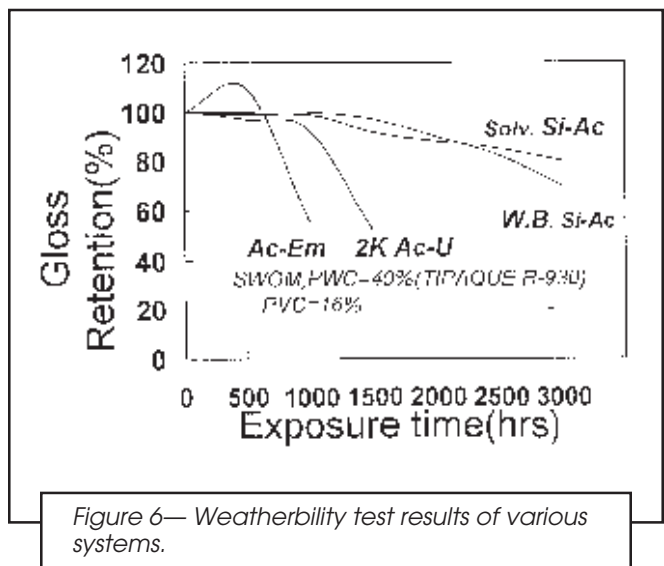
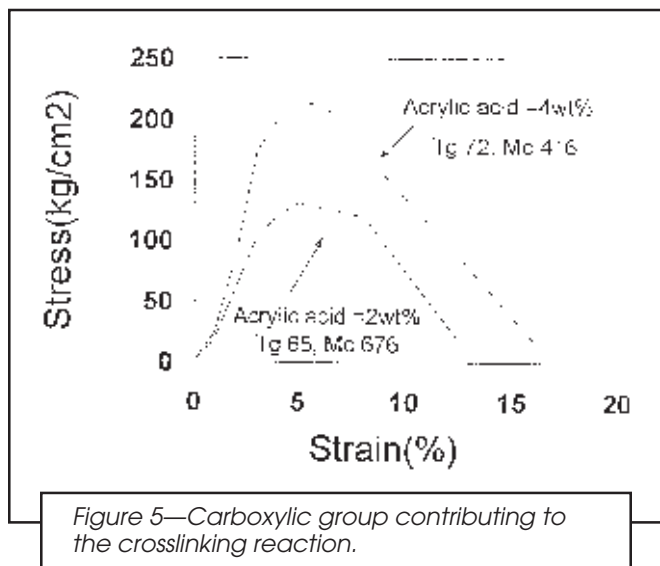


Table 4—Distribution of Si Atom<sup>a</sup> in the Film

Plate	Surface (Air)/Film	Inside Film	Reverse Film/(Plate)	Interface (Film)/Plate
Aluminum.....	0.4	0.9	2.2	0.4
Polypropylene .....	0.6	0.6	0.7	—

(a) Atom %: analyzed by XPS.

addition, the glass transition temperature ( $T_g$ ) and the crosslinking density ( $1/M_c$ ) increase with the increase in the content of carboxylic acid groups. This suggests that the carboxylic acid group contributes to the crosslinking reaction even at room temperature.

In conclusion, the results presented indicate that the crosslinking reactions in this curing system are preferable to the WB ambient curing system.

For the selection of silicone compounds, the crosslinkability of the varied "Epoxy-Silane" hardener cured with Model Compound B was measured (Table 1). The condensed hardeners show lower reactivity than the monomeric epoxy-silane hardener.

These results suggest that the condensation reaction on the silyl group and on the epoxy group site of the monomeric epoxy-silane proceed at the same time, since, if the condensation reaction was completed before the reaction on the epoxy group site, the crosslinkability would be expected to be lower than it is.

Concerning the "pot-life" at room temperature after mixing Model Compound B with epoxy-silane hardeners, the composition using the monomeric epoxy-silane hardeners has a longer pot-life (24-48 hr) than those using the condensed hardeners (<5 hr).

These results indicate that the condensed hardeners react only at the surface of the particles of Model B (waterborne dispersion type) to shorten the pot-life and to lower the gel-fraction. On the other hand, some molecules of the monomeric hardeners react at the surface of the particles and the others can penetrate and react in the particles. Therefore, the monomeric hardeners can provide relatively longer pot-life and better MEK resistance (Table 1).

### Film Properties

We have developed a new WB silicone-acrylic resin system employing this crosslinking technology.<sup>15</sup> The paint formulations and the basic film properties of the system are compared with other systems in Tables 2 and 3, respectively.

The film made from the WB silicone-acrylic resin system shows similar film properties to the conventional 2K

solvent type such as the solvent silicone-acrylic resin system and the acrylic urethane systems and better film appearance and higher hardness than the acrylic emulsion. Furthermore, the WB silicone acrylic resin system provides good adhesion—as good as the solvent type silicone-acrylic resin. The cured film made from the WB silicone-acrylic resin system shows a "self-stratification" structure in the film when applied on metal plates,<sup>1</sup> as shown in Table 4. Composition C described earlier in this paper was applied on each substrate and cured at room temperature for seven days. The coated films were submitted to XPS (X-ray photo electron spectroscopy) analysis.

The Si atom of the hardener tends to concentrate at the interface between the film and aluminum plate. It is considered that the epoxy-silane compound as the hardener in this system works as a coupling agent between the film matrix and the metal substrate, resulting in excellent adhesion as shown in Table 3.

With weatherability, the WB silicone-acrylic resin system shows better performance than the conventional acrylic emulsion and the 2K acrylic urethane system as shown in Figure 6.

## CONCLUSION

The crosslinking behavior of the silicone-acrylic resin system has been explicated in the course of this study. We are convinced that the silicone-acrylic resins system using the crosslinking technology described here can overcome at least some of the defects of conventional waterborne systems.

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