Silanes in High-Solids and Waterborne Coatings

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INTRODUCTION

vdrolyzable organofunctional silanes (OFS) have played an important role as crosslinkers, both in Lisilicone elastomers chemistry and in organic polymer technology.^{1,2} These silvlated polymers are crosslinked and cured with moisture from the air to form siloxane bonds and to give a network material. The ability of silanes added to a coating formulation to migrate to the substrate/coating interface and improve bonding is well known.¹ Generally, the substrates can be metal, mineral or plastic surfaces, glass or ceramic fibers, and fillers. The easy hydrolysis of these groups and subsequent condensation of the resulting silanols to form siloxane bonds are the chemical basis for the functional roles of coupling and crosslinking. The kinetics and fundamental aspects of alkoxy silane hydrolysis and condensation were previously reviewed.3 Some advancements in using silanes in high-solids and waterborne coating technologies are introduced in this paper.

Silanes in High-Solids Systems

In our laboratories, we have explored the benefits of OFS crosslinking to provide mar resistance to solventborne acrylic automotive clearcoats. Possible mechanisms are presented in this study. The mar resistance of an organic coating defined by Corcoran is its ability to withstand scratching and scuffing actions.⁴ Abrasion resistance may be defined generally as the ability of a material to withstand mechanical action, such as rubbing, scraping, or erosion.⁵ Mar resistance is primarily a surface property, whereas abrasion resistance involves the body of the material as well. The following models have been proposed for abrasive wear:

BRITTLE POLYMERS: The wear volume V_w can be determined as follows^{6,a,b}:

$$V_{w} = k_{1} L \bullet d \bullet \tan \Theta / \pi H$$
 (1)

Ratner has further determined the wear volume^{6c}:

$$V_{w} - k_{2} \mu \bullet d / H \bullet \sigma \bullet \epsilon$$
 (2)

Silanes have been used effectively in solventbased or waterborne coatings to crosslink binder resins, increase pigment dispersion and improve end use properties, such as mar and solvent resistance and durability. A series of silylated styrene acrylic clearcoats have been prepared and studied in order to understand the chemical and physical parameters that influence the mar resistance and weathering properties of the cured coatings. It was found that the silane content affects the indentation hardness, coefficient of friction, modulus, and toughness of the cured coatings. A relationship between these coating characteristics and mar resistance is demonstrated. In water dispersed and emulsion polymer systems, silanes maximize properties, such as adhesion and solvent resistance. Silanes are incorporated into these systems via copolymerization or post addition. Recent advances in waterborne silane technologies are discussed, including methods of improving formulation stability.

Based on the fracture energy in the fracture of metals and brittle polymers, $^{\rm 6d}$

$$V_w = k_3 (P \bullet L^{3/2} / G_{lc} \bullet H^{3/2}) d$$
 (3)

DUCTILE POLYMERS: Rice introduced the ductile fracture energy to the equation^{6e}

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Table 1—Synthesis of Methyl Methacrylate/Butyl Acrylate/ Styrene/3-Methacryloxypropyltrimethoxysilane/3-Mercaptopropyltrimethoxysilane Copolymer Resin

Ingredient Parts	by Weight
<u>Vessel</u> Butyl acetate VM&P Naphtha Toluene	336 144 96
<u>Charge I</u> Methyl methacrylate Butyl acrylate Styrene 3-Methacryloxypropyltrimethoxysilane	896 448 560 360
<u>Charge II</u> Butyl acetate Di-tert-butyl peroxide	192 112
<u>Charge III</u> Butyl acetate 3-Mercaptopropyltrimethoxysilane	192 112



Table 2—Physico-Chemical Characteristics of Methyl Methacrylate/Butyl Acrylate/Styrene/3-Methacryloxypropyltrimethoxysilane/3-Mercaptopropyltrimethoxysilane Copolymer Resin

Property	Silylated	Acrylic Resins	
Silane (wt%)	9%	14%	19%
Mp	8106	8482	8935
Mn	5219	4981	4598
Mw	7990	8379	9452
Polydispersity	1.53	1.68	2.06
Solid content	67.9%	67.3%	71.1%
Viscosity (centipoise)	3160	2405	2400
Acid number			
(mg KOH/g)	0.04	0.08	0.03
T _a	25.7°C	16.2°C	-22.4°C
²⁹ Si solution NMR			
T ⁰	100.0%	100.0%	96.6%
Τ'			3.4%

¹The weight ratio of MMA/BA/styrene/A-174/A-189/DTBP for 9, 14, and 19% silane copolymers are 45.9/18.0/22.5/4.5/4.5, 41.4/18.0/22.5/9.14/4.5/4.5 and 36.0/18.0/22.5/14.5/4.5, respectively. Methyl methacrylate was added to compensate the amount of difference. "T" represents three oxygen and one organic group tetrahedra, T = Si(O_{1/2})₂R. T⁰ represents species when no oxygen is involved in a SiOSi bridge. T¹ represents species with one bridging oxygen.

$$V_w = k_4 (P \bullet L^{3/2} / J_{lc} \bullet H^{3/2}) d$$
 (4)

where $k_{n(n=1-4)}$ = wear constant, L = normal load, H = hardness, Θ = mean slopes of asperities, d = sliding distance, μ = friction coefficient, σ = breaking stress, ε = elongation at break, G_{Ic} = fracture energy, P = yield strain, J_{Ic} = ductile fracture energy.

The ideal mar resistant materials should possess somewhat contradictory properties of the hardness of brittle materials and also the toughness of ductile materials. We report here on some of the evaluations experimentally.

EXPERIMENTAL

Characteristics of Silylated Acrylic Clearcoats

The synthesis according to the literature⁷ of the methyl methacrylate/butyl acrylate/styrene/3-methacryloxy-propyltrimethoxysilane (Silquest[®] A-174)/3-mercapto-propyltrimethoxysilane (A-189) copolymers, provided resin for the formulations of automotive clear topcoats.

Into a reaction kettle equipped with a nitrogen inlet, stirrer, reflux condenser, and three metering pumps, were charged butyl acetate, VM&P naphtha, and toluene. The solvent was heated to reflux at about 119°C. At this time, three charges of solutions (charge I, II, and III) were added simultaneously through metering pumps separately over a period of two hours. After the end of the addition, another nine parts of the peroxide catalyst were added and the solution was kept at 119°C for one hour. Then, another nine parts of the peroxide catalyst were added, and the mixture was held for another 1.5 hr at reflux.

Table 1 lists the ingredients and synthesis procedure, which gave 19% of silanes by weight. By varying the weight of 3-methacryloxypropyltrimethoxysilane and compensating with methyl methacrylate, copolymers with 9 and 14% silane were also synthesized.

The physico-chemical characteristics of these copolymers, including peak molecular weight (Mp), weightaverage molecular weight (Mw), number-average molecular weight (Mn), polydispersity, acid value, viscosity, solid content, glass transition temperature (T_g), and T^0 and T^1 by solution ²⁹Si NMR, were determined and listed in *Table* 2. The T_g s of the dried resins were measured by differential scanning calorimetry (DuPont 2100 DSC) under nitrogen. It was found that the T_g decreased when the silane concentration was increased.

Clearcoat free films were prepared according to a published formulation.⁷ The material properties of silane interpolymer free films were determined as follows: free films were prepared in aluminum molds with mold release agent (fluorocarbon release agent dry lubricant, MS-122, by Miller-Stephenson Chemical Company) or teflon molds. The film thickness was approximately 1270 μ in thickness. The tensile properties of polymer films were carried out by an Instron series IX automated materials testing system with a 4500 series interface. The crosshead speed was tested at 5 in./min.

Coating Tests

Pencil hardness, indentation hardness (by Shore durometer "A2"), and Sward hardness were determined according to ASTM 3363-74, D 2240-86, and D 2134-66, respectively. Gloss at 20° and 60° was measured by a micro-TRI-gloss reflectometer according to ASTM D 2457. Adhesion test was carried out by use of a cross-cut paint adhesion test kit (ASTM D 2197-E86). Viscosity was conducted on a Brookfield viscometer according to ASTM D 2196-86. The percent elongation for specimens on Bonderite treated cold-rolled steel panels was determined by a conical mandrel according to ASTM D 522-88. Slip angle and coefficient of friction of various coatings were determined on a Tilt Table Lubricity Tester (from American Glass Research, Inc.) according to ASTM D 4518-87. Abrasion test was conducted by a Taber Abraser model 174, using a pair of CS-10 abrasive wheels and 500 g load (ASTM D 4060-90). Mar resistance was measured by gloss retention after abrasion for 10 cycles by an AATCC Crockmeter (from Atlas Electric Devices Company, Model CM-5) wrapped with a piece of wool.

RESULTS AND DISCUSSION

Tensile Properties, Siloxane Crosslinking, and Coating Properties

The stress-strain curves of these silvlated acrylic free films are depicted in Figure 1. The moduli and toughness of the polymer films were increased by increasing the concentration of the silane crosslinker. The longterm siloxane crosslinking of the films prepared from the silvlated clearcoats was further studied by solid state ²⁹Si NMR. Notations for the types of silicon-based tetrahedra containing oxygen and organic "R" groups are defined here. "T" represents three oxygen and one organic group tetrahedra, T - Si $(O_{1/2})_3$ R. T⁰ represents species when no oxygen is involved in a SiOSi bridge. T^1 , T^2 , and T^3 represent species with one, two, and three bridging oxygens, respectively. The concentrations of T^0 , T^1 , T^2 , and T^3 were calculated from deconvoluted spectra. The "percent of crosslinking," defined as $(T^{1}+2T^{2}+3T^{3})/3$ was calculated. The cure chemistry of the clearcoats is shown in *Figure* 2 by plotting the T^0 , T^1 , T², T³ species and percentage of crosslinking versus the curing time. The values of percent of crosslinking at 49 days and 342 days were essentially the same (73.1% and 73.5%). The crosslinking rate of silane interpolymers becomes much slower after curing at ambient conditions for 10 days.

The coatings were drawn down on zinc phosphate treated steel panels and fully cured by exposure to 23°C and 50% RH for one week before testing the following coating properties on panels were determined. *Table 3* lists the results. It is interesting to note that the indentation hardness data give a distinct trend, which is consistent with the mathematical models.

During preparation of silvlated acrylic copolymers, 4.5% of mercaptosilane was incorporated as a chain transfer agent to control the molecular weight. Without the mercaptosilane, the viscosity of the copolymer was raised



Table 3—Film Properties of Silylated Acrylic Clearcoats

Test Method	Silylated Acrylic	Clearcoats
Silane (wt%) 99 Pencil hardness H Gloss (20°) 83 (60°) 94 Sward hardness 30 D.O.I. 84 Shore hardness 21	% 14% B F 3 89 4 99 0 26 5 90 5 49	19% HB 85 96 27 85 89
Tape adhesionOiElongation3.Coef. of friction0.Taber abrasion index22	B OB .7% 6.9% .53 0.31 2 19	0B 3.0% 0.24 17

The coatings were prepared on phosphate-treated panels. The abrasion test was conducted on films drawn down on E-coated panels by a Taber Abraser model 174, using a pair of CS-10 abrasive wheels and 500 g load (ASTM D 4060).



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Table 4—Coating Properties of Difunctional and Trifunctional
Silane-Containing Styrene-Acrylic Clear Coats During QUV
Aging Process ^a

_	Clearcoat		
Test Method	Α	В	С
Pencil Hardness			
0 weeks	2H	2H	6H
2 weeks	2H	2H	6H
4 weeks	7H	2H	6H
8 weeks	7H	4H	6H
12 weeks	7H	6H	6H
Adhesion by Tape Test			
2 weeks	2B	2B	3B
4 weeks	2B	2B	_
12 weeks	5B	5B	5B
Flexibility Test by			
2 weeks	3.8	3.7	3.5
4 weeks	3.6	4.2	3.8
8 weeks	6.1	7.1	3.3
12 weeks	12.9	12.8	11.9

(a) The accelerated weathering was carried out in a QUV apparatus (The Q-Panel Co.). Each weathering cycle consisted of a dry period (UV-B lamp 313 for 4 hr at 60°C) and a wet period (condensation for 4 hr at 40°C).
 (b) A: 19% A-174/A-189 (14.5% A-174 and 4.5% A-189); B: 19% MPMDM/A-174/A-

(b) A: 19% A-174/A-189 (14.5% A-174 and 4.5% A-189); B: 19% MPMDM/A-174/A-189 (4.8% MPMDM, 9.6% A-174 and 4.5% A-189); C: 14% MPMDM/A-189 (9.1% MPMDM and 4.5% A-189). Methyl methacrylate was added to compensate the amount of difference.



Table 6—Ingredients of 4 mole% Vinyltris(isopropoxy)silane Silylated Vinyl Acrylic Latex

Latex Polymer Contents Pc	arts by Weight
Vinyl acetate Butyl acrylate Vinyltris(isopropoxy)silane Water Igepal CA-897 Igepal CA-630 NaHCO ₃ Natrosol 250 MXR NH ₄ S ₂ O ₈ Abex EP-110 t-Butyl hydroperoxide-70 2% Sodium formaldehyde sulfoxylate Ammonium hydroxide	385.0 65.0 46.6 438.9 26.5 3.0 2.0 2.5 1.8 3.6 0.1 25.0 to pH 7.5
Ammonium hydroxide	to pH 7.5





Table 5—Gla	ass Transition Tempe	eratures of Cured I	Films Cast from
Silylated Acr	ylic Clearcoats ^a		

A—19% A-174/A-189; B—19% MPMDM/A-174/A-189; C—14% MPMDM/A-174/A-189						
Testing A B C						
T _g (°C)	49.7	45.7	41.5			

(a) The $\rm T_gs$ of the above free films of 50 mil thickness, cured at ambient conditions for 10 weeks, are determined by dynamic mechanical analysis.

to one million centipoise. Therefore, a control polymer with 0% silane is not feasible.

Correlation of Modulus, Friction, and Hardness on Mar Resistance of Clearcoats

The abrasion tests show decreasing Taber abrasion with increasing silane concentration. The contributions of modulus, coefficient of friction, and hardness to abrasion and mar resistance are presented individually in *Figures* 3-5. The plots illustrate that modulus and indentation hardness are inversely correlated with the rate of abrasion, whereas the coefficient of friction has a direct correlation with the rate of abrasion. By plotting the abrasion index against the empirical parameters $\mu/H \cdot \sigma \cdot \epsilon$, the consistency of the factors is further demonstrated in *Figure* 6.

The Influence of Difunctional Silane Ester on Clearcoats

Silylated acrylic clearcoats containing 3-methacryloxypropylmethyldimethoxysilane (MPMDM) were synthesized in the same manner. The free films were cured at 23°C and 50% RH for seven days. Comparisons on tensile curves among 14% MPMDM/A-189 (A), 14% A-174/A-189 (B) and a blend of A/B at weight ratio of 20/

80 are depicted in Figure 7. The weathering resistance of these clearcoats studied by QUV exposure over 2,000 hr is further described in Table 4, and in Figures 8 and 9. During this study, no crack formation was found and adhesion was actually improved. The mar resistance of these coatings was maintained after accelerated aging by QUV. Samples were coated on phosphate treated steel panels. The T_ss of free films containing difunctional and trifunctional silanes are reported in Table 5. The incorporation of a difunctional silane ester gives benefits in controlling the mechanical properties of the coatings.

Silanes in Waterborne Systems

OFS may be incorporated in latex systems by copolymerization, grafting, physical addition, or combinations. When levels rise much above 0.25% to 0.5% by weight of solids, premature crosslinking often occurs, producing a poor quality latex. Bourne et al.⁸ describes many attempts to prepare latexes containing 5 wt% and higher silane co-monomers. Masuda et al. reported using water insoluble tin catalyst in long-chain alkoxysilane silylated latexes.⁹ We report sucTable 7—Ingredients of 6 mole% 3-Methacryloxypropyltriisopropoxysilane Acrylic Latex

Latex Polymer Contents	Parts by Weight
Portion 1 Deionized water Igepal CA-897 Butyl acrylate Methyl methacrylate Methacrylic acid 3-Methacryloxypropyltriisopropoxysilane 0.15% Ferrous sulfate Potassium persulfate	479.4 44.0 55.0 120.8 2.8 41.8 6.0 3.0
Portion 2 2% Sodium formaldehyde sulfoxylate	12.0
Portion 3 Butyl acrylate Methyl methacrylate Methacrylic acid 3-Methacryloxypropyltrimethoxysilane	65.0 121.4 2.8 27.8
Portion 4 2% Sodium formaldehyde sulfoxylate	12.0
Portion 5 t-Butyl hydroperoxide-70	0.1
Portion 6 2% Sodium formaldehvde sulfoxylate	6.0

Table 8—Film Properties of Silylated Acrylic Latexes vs. Controls Without Silane

Ingredient A	В	с	D
Latex solids (wt%)	47	43	43
Butyl acrylate	26	32	32
Methyl methacrylate 67	67	67	67
Methacrylic acid	2	2	2
triisopropoxysilane	6	0	0
Catalyst ^a No Film Properties	Yes	No	Yes
Gloss (60°)	83	84	83
Pencil hardness	H 5B >400	B 5B 10	HB 5B 30

(a) Tyzor® 131 (5%) was used as the catalyst. Coatings were prepared from fresh mixtures of Tyzor catalyst and the acrylic latexes. Six percent of diethylene glycol monobutyl ether acetate was added as coalescent. Coatings were baked at 250°F for 20 min and further cured at 23°C and 50% RH for seven days.

Table 9—Film Properties of the Silylated Vinyl Acrylic Latexes vs. Controls Without Silane

Ingredient A	В	С	D
Latex solids (wt%)	53	51	51
Vinyl acetate	86	86	86
Butyl acrylate 10	10	14	14
Vinyltris(isopropoxy)silane	4	0	0
Catalyst ^a No	Yes	No	Yes
Film Properties			
Gloss (60°)	86	82	103
Pencil hardness 3B	В	4B	4B
Tape adhesion 5B	5B	5B	5B
MÉK double rubs 17	50	19	15

(a) Tyzor 131 (5%) was used as the catalyst. The silylated vinyl acrylic latexes with 5% Tyzor 131 catalyst were stored at room temperature for four weeks. Coatings were baked at 250°F for 20 min and further cured at 23°C and 50% RH for seven days.



Table 10—NMP Paint Adhesion Test Results of Vinyl Acrylic Latex Films Cast from Polymer Containing 1.0%-3-Methacryloxypropyltriisobutoxysilane vs. Concentrations of Titanate Catalysts^a

Catalyst		NMP Paint Adh Catalyst Co	esion ^b (Minute oncentration	es)
	0.05%	0.5%	1%	2%
Tyzor 131 Tyzor LA	5.5 5.6		 39	 56

(a) The film thickness was 2 mils. The values were average values taken out of three coated stainless steel panels. Coatings were baked at 121°C for 20 min, then further cured at 23°C and 50% RH for seven days.

(b) The adhesion at the paint-metal interface was determined by the use of N-methyl pyrrolidone (NMP) heated at 60°C. In all cases, a 2.0 cm² sample was immersed in NMP and the time for paint removal was noted.



cessful attempts to incorporate silanes at 10% and higher levels.

The principles in our work involved the use of hindered, slow-to-hydrolyze alkoxy silanes, together with catalysts selected for good performance and for in-can stability.

EXPERIMENTAL

Preparation of Silylated Vinyl Acrylic Latexes

The synthesis ingredients for silylated vinyl acrylic latex (9.4% silane) is shown in *Table* 6. The procedure is as follows:

Deionized water, IGEPAL CA-897 and IGEPAL CA-630 surfactants (from Rhône-Poulenc), sodium bicarbonate and Natrosol 250 MXR (from Aqualon) were charged to a reactor equipped with a condenser and a stirrer. The system was heated to 65°C with a heating mantle and purged with nitrogen. Ammonium persulfate and ABEX EP-110 (from Rhône-Poulenc) were added. Monomer feed was started. After the seeded latex was formed by adding the first 10% of the monomer blend and reacting for 15 min, the remaining monomer mixture was added over three hours at 75°C. In the presence of t-butyl hydroperoxide-sodium formaldehyde sulfoxylate, reaction was continued for another hour to complete polymerization. Ammonium hydroxide was used to adjust the pH of the latex to 7.5 before straining.

The synthesis ingredients for a silylated acrylic latex (19% silane) is shown in *Table* 7. The procedure is described as follows:

Into a one-liter reaction vessel equipped with a stirrer, thermometer, dropping funnel, and nitrogen gas inlet were charged deionized water (479.4 g), IGEPAL CA-897 (44 g, from Rhône-Poulenc), butyl acrylate (55.0 g), methyl methacrylate (120.8 g), methacrylic acid (2.8 g), 3-methacryloxypropyltriisopropoxysilane (41.8 g), aqueous 0.15% ferrous sulfate solution (6.0 g), and potassium persulfate (3.0 g) at ambient temperature. They were mixed for five minutes. A two percent aqueous solution of sodium formaldehyde sulfoxylate (12.0 g) was added. The exotherm increased the temperature from ambient to 60° to 65°C. The mixture was cooled to 35°C. A second mixture of butyl acrylate (65.0 g), methyl methacrylate (121.4 g), methacrylic acid (2.8 g), and 3-methacryloxypropyltriisopropoxysilane (27.8 g) was added to the reaction vessel. A second charge of a two percent aqueous solution of sodium formaldehyde sulfoxylate (12.0 g) was added to the reaction vessel. The mixture was allowed to heat up to a temperature of 60° to 65°C, and then cooled to 50°C. Then t-butyl hydroperoxide-70 (0.1 g) was slowly added to the reaction mixture followed by a two percent sodium formaldehyde sulfoxylate solution (6.0 g). The reaction mixture was stirred and then cooled to room temperature. Concentrated ammonium hydroxide solution was used to adjust the pH of the silvlated polymer emulsion to 7.5.

RESULTS AND DISCUSSION

Stable Silylated Acrylic and Vinyl Acrylic Latexes

The alkoxy groups included selected hindered or long alkoxy chains, such as iso-propoxy, n-butoxy, i-butoxy, n-octoxy. Concentrations of silane co-monomers ranged from 0.2 to 24 wt%, or up to 8 mole%. Stable, aqueous emulsion copolymers with alkoxysilane crosslinking functionality were prepared by emulsion polymerization. In order to balance the reactivity of co-monomers, the silvlated vinyl acrylic latex was prepared by a semicontinuous batch process. The silvlated acrylic latex was prepared by a two-staged batch process. These systems showed no seeding or viscosity increase after 12 months of room temperature storage. Solution ²⁹Si NMR detected only the T⁰ species at a seven-month room temperature storage. In contrast, latexes containing methoxy or ethoxy silanes at levels greater than five percent gel during preparation or with a few days of room temperature storage.

Performance Improvements of Silylated Emulsion Polymer Coatings

Tables 8 and 9 show the performance improvement created by silane incorporation. The silvlated acrylic latexes demonstrate a self-curing system which may not require an organometallic catalyst. The methacrylic acid co-monomer, which may function as an acid catalyst at the film forming stage, may play an important role in this self-curing system. When the fugitive base evaporates and the system moves to acidic pH, the conditions favor the hydrolysis and condensation reactions of the hindered silanes. Alternatively, water soluble or dispersible organotitanates and organotins are compatible with the silvlated emulsion polymers in one-pack systems. As shown in Table 9, the presence of the watersoluble chelated titanate catalyst, Tyzor[®] 131, in the silvlated vinyl acrylic system which contains no acid copolymer does accelerate the siloxane crosslinking and solvent resistance.

Effects of Catalysts in the Silylated Vinyl Acrylic Systems

Moving from a solvent system to a waterborne system, the choice of cure catalyst and its compatibility with latexes are crucial. *Figure* 10 depicts the effect of titanate concentration on the solvent resistance of the 1.0% 3-methacryloxypropyltriisobutoxysilane silylated vinyl acrylic latex coating. The results show that controls without silane in the latexes do not show enhanced solvent resistance, even with catalyst. The NMP paint adhesion¹⁰ at the paint-metal interface was evaluated on the same latex in the presence of various concentrations of titanate catalysts (see *Table* 10). The adhesion at the paint-metal interface was enhanced by increasing the concentration of water-miscible titanate catalysts.

Further studies on the catalytic effects and the stability of a one-pack system silvlated latex containing a







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Table 11—Solvent Resistance of Films Cast from Vinyl Acrylic Latexes Containing 4 mole% of Silanes and 5% Tyzor 131 vs. the Storage Time of the Admixtures^a

	MEK Double Rubs (times) Storage Time				
Silane in Latexes with Tyzor 131 0	2 Weeks	4 Weeks	8 Weeks	15 Months	
3-Methacryloxypropyltriisopropoxysilane	80	119	99	157	
3-Methacryloxypropyltriisobutoxysilane	97	122	125	251	
3-Methacryloxypropyltrioctoxysilane	81	103	128	19	
Vinyltriisobutoxysilane	74	100	97	255	
Vinyltri-t-butoxysilane	47	75	67	8	

(a)Tyzor 131 is a catalyst from DuPont. The silvlated vinyl acrylic latexes with 5% Tyzor 131 were stored at room temperature. At a determined time, portions of these latexes were taken in preparing the films. No gel or seeding was noted. MEX resistance of the coatings was conducted according to ASTM D 4752-87. The film thickness was 2 mils. The values were determined by averaging three data points tested on the same steel panels. Coatings were baked at 121°C for 20 min and further cured at 23°C and 50% RH for seven days.

Table 12—Solvent Resistance of Films Cast from 4 mole% 3-Methacryloxypropyltrioctoxysilane Vinyl Acrylic Latex Film in the Presence of Various Organotin Catalysts, after Curing at Room Temperature and at 121°C^a

Catalyst	MEK Double Rubs (times)		
	RT	Baked	
Fomrez [®] UL-1	39	51	
Fomrez [®] UL-22	48	53	
Fomrez [®] UL-32	41	49	
No catalyst	15	19	

(a) Fomrez[®] UL-1, UL-22 and UL-32 are organotin catalysts from Witco Corporation. MEK resistance of the coatings was conducted according to ASTM D 4752-87. The film thickness was 2 mils. The values were determined by averaging three data points tested on the same steel panel. Coatings were baked at 121°C for 20 min and/or cured at 23°C and 50% RH for seven days.

Table 13—Gel Contents of the Solid Films Made from Vinyl Acrylic Latexes Containing Various Silanes with and without a Titanate Catalyst

	Gel Content (%)			
Type of Silane in Latex	No Catalyst ^a	With Titanate ^b		
3-Methacryloxypropyl triisopropoxysilane		25.4		
3-Methacryloxypropyl triisobutoxysilane 3-Methacryloxypropyl		75.6		
trioctoxysilane Vinyltriisobutoxysilane Vinyltris(t-butoxy)silane		78.3 53.1 0		

(a) The silylated vinyl acrylic copolymer films were cast from freshly made 4 mole % silane-containing latexes without catalyst. The films were further cured at ambient conditions for 10 weeks. The gel content is the amount (in wt%) of polymer remaining after being swallen in solvent (MEK).

(b) The silylated vinyl acrylic copolymer films were cast from 4 mole % silanecontaining latexes with 5% Tyzor 131, which were stored at ambient condition for eight weeks. The films were further cured at ambient condition for 10 days. catalyst, have been carried out. Mixtures of various silane-modified silylated vinyl acrylic latexes with 4 mole% silanes and 5 wt% Tyzor[®] 131 were prepared. The solvent resistance represented by MEK double rub data for these films versus storage period (up to 15 months) is described in *Table* 11. Hindered silanes with isopropoxy or isobutoxy groups put considerable steric hinderance adjacent to the silicon atom generating hydrolytic stability. They work well in silylated polymer/catalyst onepack systems. The bulky t-butoxy group hinders the silicon atom so severely it is hard to hydrolyze/cure even with a catalyst. The long chain silane with octoxy group performs well in a two-pack system due to its higher reactivity for hydrolysis. Water-stable tin catalysts are also effective (*Table* 12).

Siloxane Crosslinkage of Silylated Vinyl Acrylic Films

The siloxane crosslinking of vinyl acrylic films containing 10 wt% of various silanes were studied by solid state ²⁹Si NMR. The percent of crosslinking, T⁰, T¹, T², and T³ are presented in *Figure* 11. Solid powder prepared from a 10 wt% 3-methacryloxypropyltrimethoxysilane gel was also investigated for a comparison. It is concluded that in the absence of a catalyst, the percent of siloxane crosslinks among the films increases according to the order: vinyltriisobutoxysilane < 3methacryloxypropyltriisopropoxysilane < 3-methacryloxypropyltriisobutoxysilane < 3-methacryloxpropyltrioctoxysilane < 3-methacryloxypropyltrimethoxysilane.

The gel contents of the coatings of vinyl acrylic latexes containing various silanes with and without titanate catalysts are described in *Table* 13. In the presence of a titanate catalyst, the gel contents of the latexes were enhanced, except for the extremely unreactive vinyltris(tbutoxy)silane-containing latex.

CONCLUSIONS

By increasing the concentrations of silanes, the mar and abrasion resistance properties of automotive clearcoats are improved. The rate of abrasion correlated directly with coefficient of friction and inversely with hardness, modulus, and toughness. The crosslinking rate becomes

much slower after curing for 10 days. Silylated acrylic clearcoats cured at ambient conditions for one year afford approximately 75% of the total potential crosslinks.

Stable, aqueous emulsion copolymers with hindered alkoxysilane crosslinking functionality were achieved. OFS serve as "latent crosslinking monomers," crosslinking the polymer upon subsequent complete drying of the latex particles. The monomeric acid containing silylated acrylic latex provides a self-curing thermosetting latex that can be cured without added crosslinking agent. Mixtures of the silylated emulsion polymers with water miscible or dispersible organometallic catalysts did not seed or gel over a 15-month period of ambient storage. The compositions have improved properties including solvent resistance, adhesion, hardness, abrasion resistance, and mar resistance.

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