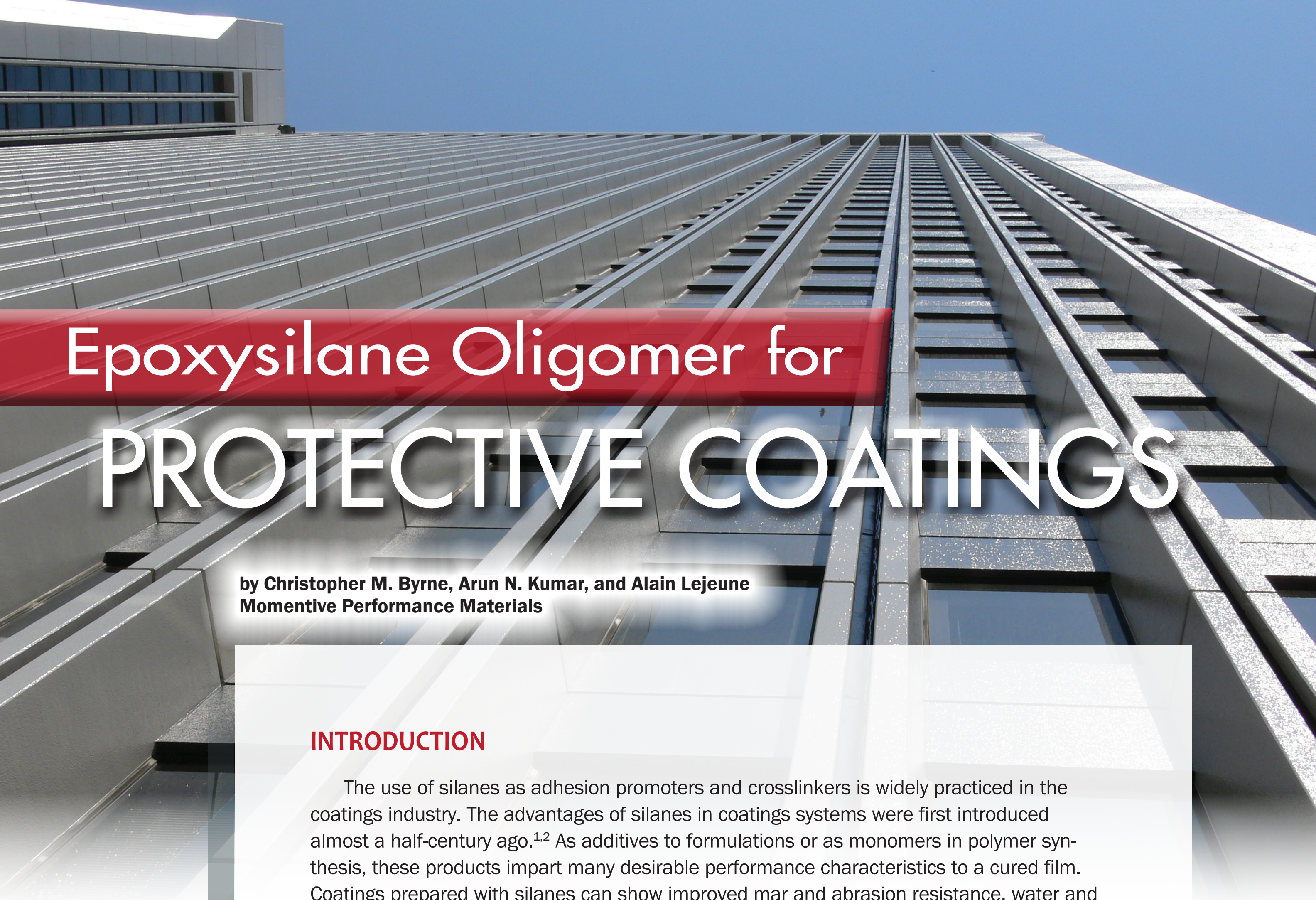

Epoxysilane Oligomer for PROTECTIVE COATINGS

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INTRODUCTION

The use of silanes as adhesion promoters and crosslinkers is widely practiced in the coatings industry. The advantages of silanes in coatings systems were first introduced almost a half-century ago.[1,2] As additives to formulations or as monomers in polymer synthesis, these products impart many desirable performance characteristics to a cured film. Coatings prepared with silanes can show improved mar and abrasion resistance, water and solvent resistance, acid and alkali resistance, and adhesion to various substrates.[3] The use of silanes in coatings, however, is not limited to interaction between the organic polymer and the substrate. Pigments pretreated with silanes show increased dispersibility and binding, resulting in lower viscosities and better hiding power. Thus, silanes have steadily grown to become an indispensable component in many aspects of the coatings industry.

Organofunctional silanes consist, in general, of an organic functionality (Y, *Figure* 1) linked through an organic spacer (R’) to one or more silicon atoms each with one, two, or

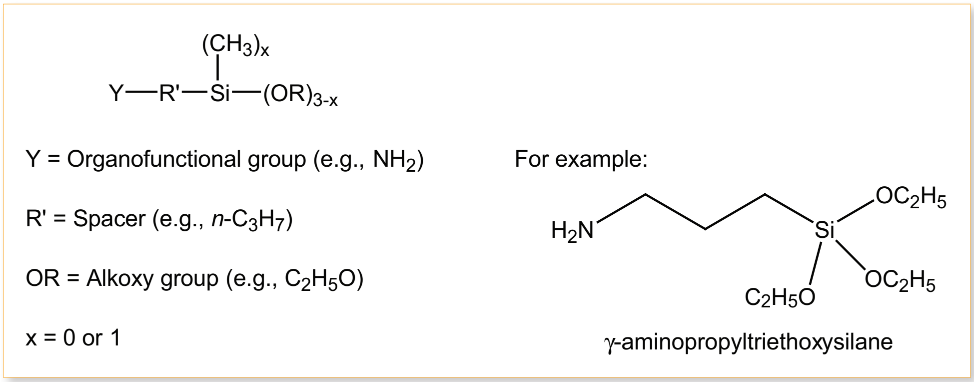

Figure 1—Anatomy of an organofunctional silane

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Technical subject matter in this article is described and protected by one or more pending U.S. patent applications and foreign counterparts.

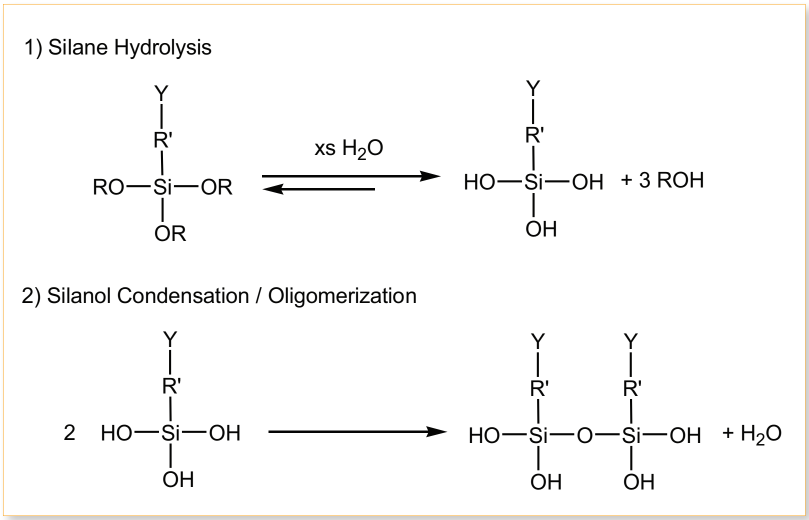

Figure 2—Controlled hydrolysis and condensation reactions for oligomerization.

three hydrolyzable alkoxy ligands (OR). The organic moiety (Y) provides a "handle" that can react with functionality on a polymer backbone. The hydrolyzable groups (OR) can react with water, forming reactive silanol groups (SiOH), and then bond to a filler or substrate or self-condense to form siloxane crosslinks (SiOSi) (*Figure* 2).

The reactivity of alkoxy substituents on silanes is sensitive to many factors, including steric hindrance, temperature, moisture content, and pH. A number of studies on the reactions and reactivity of alkoxysilanes have appeared in the literature.[4,5] When the alkoxy groups are hydrolyzed, the resulting hydrolyzate, a trisilanol species, is very reactive and will participate in two primary reactions: silanol-silanol condensation (siloxane crosslinking) and silanol-substrate coupling. These reactions are nearly indiscernible in a formulation and may take place in parallel in a polymer system.

There are numerous industrial applications of organofunctional silanes in the coatings industries. Silanes are key components in marine and protective coatings, decorative paints, industrial coatings and finishes, wood coatings, and printing inks. Depending upon the chemistry of the Y group, silanes can be incorporated into solventborne, UV-curable, and waterborne systems. Improvements induced by silanes typically include better water resistance, chemical resistance, dry and wet adhesion on metal, corrosion resistance on metal surfaces, adhesion to glass or polyolefin substrates, and coating durability.

The function of the silane varies in each system, but typically falls into one of two primary categories: crosslinker and surface modifier. In systems where water and chemical resistances or enhanced durability is desired, the silane's role in the coating is to create greater crosslink density through silanol-silanol condensation reactions. This type of coating typically requires a pre-mix step where the silane and polymer are mixed separately from other components to ensure sufficient grafting of the silane onto the polymer backbone. After the requisite induction period, the modified polymer can then be formulated with the remaining ingredients.

For improved adhesion on substrates such as metal or glass, the silane acts more as an adhesion promoter by bonding with the surface through silanol-condensation-type reactions. In ideal cases, a silane hydrolyzate solution is applied to the surface as a pretreatment and allowed to air dry or cure at elevated temperature. For particles, flakes, dusts, and the like, this can be readily accomplished by making a slurry or a paste of the particulate matter in the silane hydrolyzate (see the Methods and Materials section) or by spraying the silane hydrolyzate onto the particulates to create a functional treatment on the surface. However, for the cases where such separate steps are not feasible, the silane can be introduced at another point in the formulation of the final coating.

Typically, silane additives used in coatings applications are monomeric in nature; that is, they conform to the formula given in the previous section. However, monomeric silanes are not without limitations. They can be complicated to handle in solvent-based formulations and even more complicated to handle in waterborne formulations, where the silane is prone to hydrolysis and subsequent condensation. A key issue for the use of organofunctional silanes relates to the dual nature of the silane molecule. The organofunctional end will participate in standard organic coupling reactions whereas the trialkoxysilane portion will proceed through hydrolysis and condensation reactions. These two sets of reactions are governed by different and independent rates and this can affect the overall performance of the additive. As a result, monomeric silanes may also exhibit slow cure rates in formulated coatings, so that building film properties will require significant amounts of time, especially for room temperature applications. This point is exaggerated by the fact that monomeric silanes bear a single organofunctional group per unit of grafting or coupling. There is then greater reliance upon siloxane crosslinking to effectively deliver the physical properties desired, as the organic reaction is only half of the steps required to crosslink the matrix.

Monomeric silanes also typically have a rather high proportion of volatile organic contents (VOC) relative to their molecular weights. For example, γ-aminopropyltriethoxysilane releases 62.5% of its weight in ethanol and γ-glycidoxypropyltrimethoxysilane releases 40.7% of its weight in methanol. Both silanes contribute to the VOC of the formulations, where they can represent from 0.1 to 15% of the total. With new environmental regulations further restricting the allowable VOC content of coatings formulation, every component is under scrutiny for its contribution to the overall VOC content of the final formulation.

We sought to develop a product that would overcome these limitations and began designing and synthesizing an oligomeric silane. A silane oligomer is defined as a low molecular weight polymer where the polymerization will be made predominantly through two consecutive reactions: silane hydrolysis and silanol-silanol condensation (*Figure* 2). The inherent dilemma in the synthesis of such oligomers from monomeric silanes is exerting sufficient control over those two reactions so that the silane oligomer's molecular weight can be dictated. There are methods designed to address this issue, and controlled hydrolysis and condensation reactions can be applied to prepare oligomeric siloxane structures. An oligomeric structure addresses the issues around silane reactions as a small siloxane network has been formed prior to formulation or cure, so that coupling between the polymer and the organofunctional group represents the primary reactivity of the compound. This article aims to describe a first generation of oligomeric products based on epoxy functional groups, as epoxy-functional materials are very common in the coatings industries.

METHODS AND MATERIALS

Koenig hardness testing was performed according to ISO 1522-1973. Stain resistance testing was performed according to DIN 68861-1B.

Gel Content Determination

Gel content determination was performed using a modified ISO 579 method. In a typical procedure, the silane was mixed into neat binder at least 24 hours prior to the start of the test. The binder was applied in Teflon cups and allowed to cure for 24 hours at 80°C. The cured binder was removed from the cups and extracted for eight hours with methyl ethyl ketone in a Soxhlet apparatus. Gel content was calculated as the difference between the cured binder before and after extraction.

Hydrogen Gassing Experiments

Hydrogen gassing experiments were conducted in 50-mL brown glass containers using 50 grams of zinc slurry according to the formulations below. The glass container was placed in a heated circulation bath at 40°C. The container was then sealed with a rubber stopper and linked with a polyethylene tube to a measuring pipette filled with water. The measuring pipette was left standing and the level of liquid inside was adjusted to zero. The amount of gas generated was measured over a two-week period. Formulations for these experiments are summarized below with the procedures used for sample preparation.

Procedure for silane hydrolyzates of A-187 and MP 200

Material	A-187	MP 200
Deionized water	47.5	20.2
H_3PO_4 solution (1%)	0.0	1.8
Boric acid solution (45 g/l)	32.5	40.2
Silane	20.0	36.0
Dissolution time	3 hours	16 hours

Procedure

1. Under agitation, add H_3PO_4 and boric acid solutions to deionized water.
2. Under slow agitation, add silane.
3. Mix and allow to hydrolyze for given time.

Procedure for dispersion of silane hydrolyzates of A-187 and MP 200 silane into a waterborne epoxy-based binder

Material	A-187		MP 200	
	0.2 wt%	2.0 wt%	0.2 wt%	2.0 wt%
EPI-REZ 6520-WH-53 (Epoxy dispersion)	39.0	39.0	39.0	39.0
Deionized water	9.5	5.3	9.7	7.4
Silane hydrolyzate	0.5	4.7	0.3	2.6
Propylene glycol phenyl ether[a]	4.0	4.0	4.0	4.0
4P16 (Zinc dust)	47.0	47.0	47.0	47.0

(a) Dowanol® PPH. Dowanol® is a registered trademark of The Dow Chemical Company.

Procedure

1. Mix epoxy dispersion, deionized water, hydrolyzate, and propylene glycol phenyl ether.
2. Under agitation, add zinc dust and disperse for 10 minutes at 1500 rpm.

Procedure for dispersion of zinc dust into silane hydrolyzates of A-187 and MP 200

Material	A-187		MP 200	
	0.2 wt%	2.0 wt%	0.2 wt%	2.0 wt%
Deionized water	9.0	4.8	9.2	6.8
Silane hydrolyzate	0.5	4.7	0.3	2.6
Berol 48	0.3	0.3	0.3	0.3
Berol 50	0.2	0.2	0.2	0.2
NaOH solution (1 wt%)	0.0	0.0	0.0	0.1
4P16 (Zinc dust)	47.0	47.0	47.0	47.0
EPI-REZ 6520-WH-53 (Epoxy dispersion)	39.0	39.0	39.0	39.0
Propylene glycol phenyl ether[a]	4.0	4.0	4.0	4.0

(a) Dowanol® PPH.

Procedure

1. Under agitation, mix deionized water, silane hydrolyzate, Berol 48, and Berol 50.
2. Under agitation, add zinc dust and disperse for 10 min at 1500 rpm.
3. Add epoxy dispersion and propylene glycol phenyl ether and mix for 20 min.

RESULTS AND DISCUSSION

Epoxysilane Oligomers

The general structure of an epoxysilane oligomer (ESO) is shown in *Figure* 3. These oligomers are synthesized through the controlled hydrolysis and condensation of epoxysilanes in such a way so as to maintain certain levels of alkoxy content and preserve the reactive epoxy functional groups. These epoxy groups are subject to hydrolysis under oligomerization conditions, though this side reaction is minor and produces a small number of diol functional groups on the oligomer. With both silane and organofunctional groups available, the oligomer is still reactive for both: (1) coupling to substrates and other silanes and siloxane oligomers through the silane portion, and (2) grafting to polymer functional groups through the epoxy groups. The partial condensation of the silanes into an oligomeric form reduces the alkoxy content of the material, thus providing a benefit in VOC reduction for the overall formulation. Further, the oligomer is 100% active material without the need of added solvent. The oligomer is also less sensitive

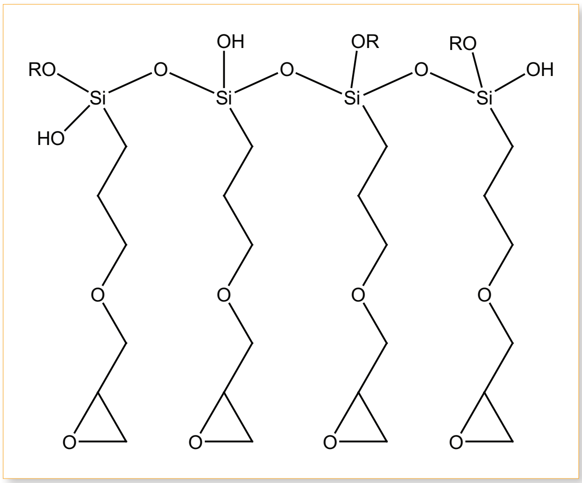

Figure 3—Schematic description of ESO structure.

to hydrolysis than a monomeric silane and can be hydrolyzed in a more controlled fashion.

A new product based on this ESO technology, called CoatOSil* MP 200 silane, has recently been introduced by Momentive Performance Materials. In this article, the product is referred to as MP 200. Comparing certain properties of this representative ESO to those of standard monomeric silanes like γ-glycidoxypropyltrimethoxy silane (Silquest A-187* silane, referred to here as A-187) and γ-glycidoxypropyltriethoxysilane (Silquest* A-1871 silane, or A-1871) gave a good representation of the types of benefits that such a structure can provide. As shown in *Table* 1, MP 200 released a lower amount of alcohol upon hydrolysis, which translated to a lower VOC for the compound. The practical implication of this is that for identical active content and loading in siloxane, the ESO liberated a significantly lower amount of alcohol. The calculation indicates that one part of A-187 would be replaced by 0.75 parts of MP 200, which would liberate only 22% of its weight in VOC. Therefore, the final VOC released by MP 200 after total hydrolysis at equal actives content was then 60% lower than the monomeric epoxysilane. The same comparison for the ethoxy version (A-1871), gave a VOC release more than 75% lower. In practice, the VOC reduction could be even higher as the efficiency of the ESO may lead to a lower loading rate in the formulation.

Another important feature of MP 200 is that it has higher epoxy content per gram of material. The greater epoxy density increases the potential crosslinking efficiency and density for the ESO in reaction processes like coupling with carboxyl, hydroxyl, or amino functionalities. This feature may also lead to faster curing rates.

Characterization of MP 200 using ^{29}Si NMR spectroscopy readily displayed the extent of condensation of the silanol groups of the ESO. The relative amounts of different species, such as silanol (SiOH), alkoxysilane (SiOR), and siloxane (SiOSi) are represented by four classifications: T^0, T^1, T^2, and T^3. These four terms each describe a particular type of SiO- bonding in the oligomer. The T^x nomenclature for bonding in trialkoxysilanes corresponds to the number of SiOSi bonds present for each silane group, where x is the number of SiOSi bonds. Therefore, a typical trialkoxysilane or trisilanol is represented by T^0, as there are no SiOSi bonds. T^3 represents a silane that is completely reacted with other silanes to give 3 SiOSi bonds. These species can be differentiated in the ^{29}Si NMR spectrum of MP 200, which is shown in *Figure* 4. MP 200 still has a significant amount of alkoxy and/or silanol groups available in the matrix, as indicated by the relative amounts of T^1 and T^2.

Potential Application Examples

ESOs may find use in many of the same applications as monomeric epoxysilanes. Their potential uses as crosslinkers for acrylic latexes and as surface modifiers for metallic particulates are discussed below.

Crosslinker for Acrylic Latexes

MP 200 can be introduced into a formulation in the same manner as a monomeric silane. In the

Table 1—Selected Properties of Monomeric Silanes and ESO MP 200.

	A-187	MP 200	A-1871
Alcohol released[a]	41%	22%	55%
Flash point[b]	110° C	107° C	110° C
Active material	>98%	>98%	>98%
Epoxy (meq/gram)	4.145	4.785	3.591
Viscosity (Temp)[c]	3 cSt (25° C)	30 cSt (25° C)	3 cSt (25° C)
Water solubility[d]	Soluble	Not soluble	Soluble

(a) % Alcohol released calculated for A-187 and A-1871 based on molecular structure.
% Alcohol released determined for MP 200 by hydrolysis in water and analysis of liberated methanol by gas chromatography.
(b) Flash point determined using closed-cup Pensky-Martens method.
(c) Viscosity was measured using a Brookfield viscometer.
(d) Water solubility determined using a 5-wt% concentration of material in deionized water.

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*CoatOSil, Silquest, and Silquest A-187 are trademarks of Momentive Performance Materials Inc.

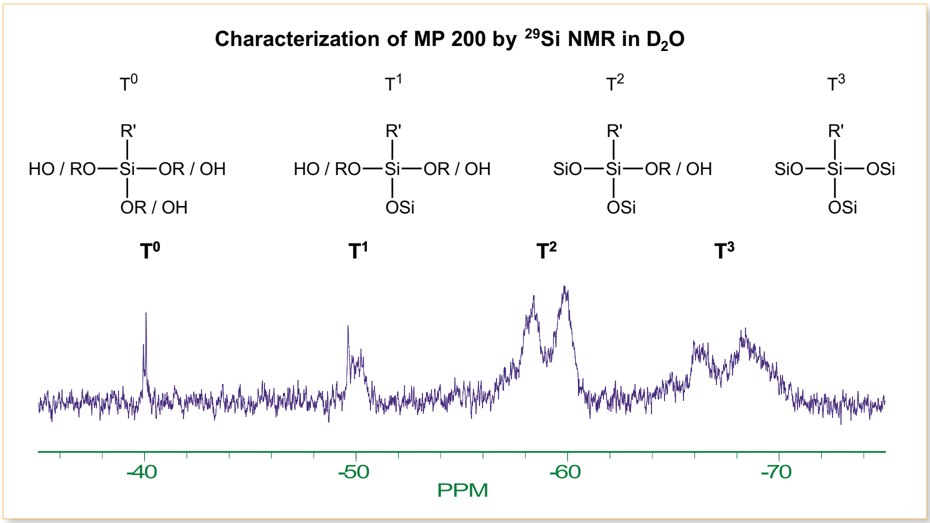
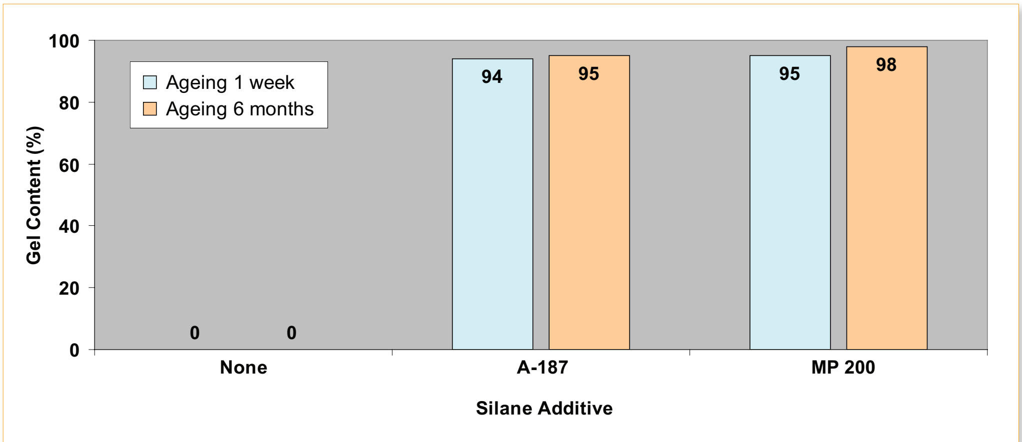


Figure 4—Typical ^{29}Si NMR spectrum of MP 200, a representative ESO.



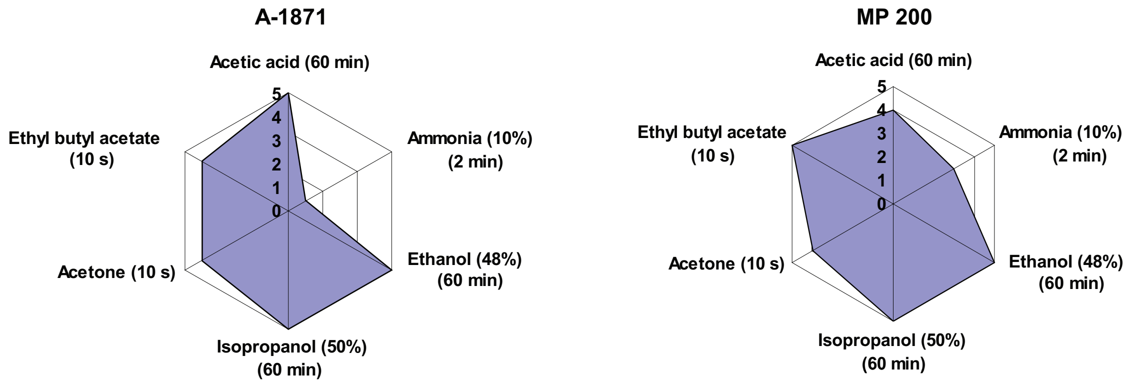
Formulation based on : Styrene-acrylic emulsion
Silane loading : 1.2 wt% A-1871, 0.9 wt% MP 200
Formulation ageing : 7 days or 6 months
Curing conditions : 15 days at RT – Coating applied on Teflon
Gel content : Modified ISO 579

Figure 5—Impact of epoxysilane monomer and ESO on gel content.

case of latexes, this was easily achieved by adding the silane to the waterborne, pre-manufactured polymers prior to formulation and allowing an induction time of approximately 24 hours. Given its hydrophobic nature, MP 200 migrates into the micelles of the latex emulsion and reacts with the acid groups of the acrylic polymer. The sample was then letdown and the performances of a styrene-acrylic latex treated with A-1871 were compared with the same styrene-acrylic latex treated with MP 200. Actual weight percent of each additive was adjusted so as to maintain the equivalent actives content for an accurate comparison. These coatings, along with the standard styrene-acrylic latex, were tested for gel content, stain resistance, and Koenig hardness.

One of the most important requirements for a coatings formulation is the extent of crosslinking in the system, as many properties are derived from this behavior. Gel content determination provides a good indication of crosslinking within the formulation, and results for this study are shown in *Figure* 5. The impact on gel content was significant for both silane-based materials. This suggested that both additives induced greater crosslink density for the matrix, though MP 200 provided slightly higher gel content. Results also showed that, even after six months of ageing, the two formulations kept their reactivity and stability, indicating that the products can be considered shelf stable. High gel content in a formulation typically correlates with improvements

Figure 6—Impact on staining resistances of monomeric epoxy silane and ESO.



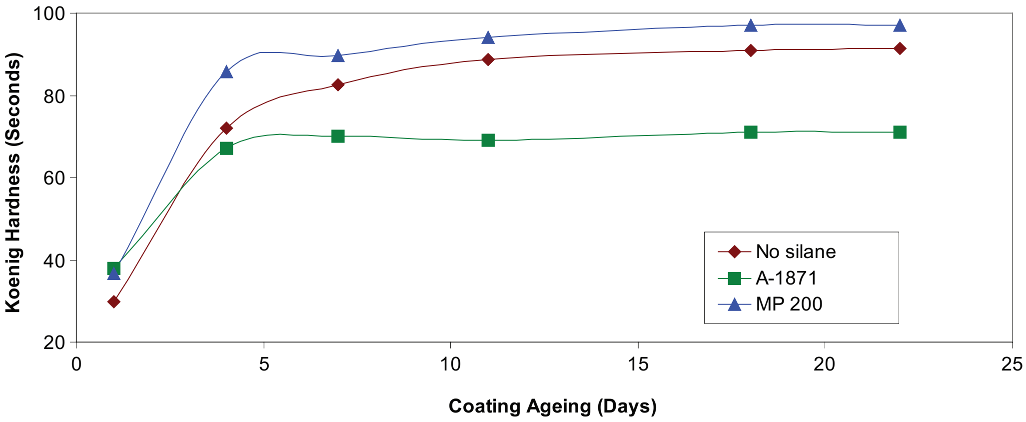
Formulation based on : Styrene-acrylic emulsion
Silane rate : 1.2 wt% A-1871; 0.9 wt% MP 200
Formulation ageing : 7 days
Curing conditions : Oak panels – Spray drying – 130 g/m^2 - 7 days at RT
Chemical resistance : DIN 68861-1B (5: Excellent, 0: Fail)

in chemical resistances for the cured coating, and this was observed through stain resistance tests (*Figure* 6). The addition of MP 200 into the styrene-acrylic latex formulation improved resistance of the coating against ammonia solution, while maintaining excellent results for the other staining agents.

Another advantage gained from the use of MP 200 in the latex formulation was shown in the results of the Koenig hardness test. This test measured the evolution of coating hardness over time. It is evident from *Figure* 7 that the ESO-treated latex built hardness more rapidly than either the control (without any additive) or the A-1871-treated formulation. Further, this formulation actually exhibited greater hardness than either of the other two samples, demonstrating the greater efficiency of crosslinking with the ESO MP 200.

The evaluation of MP 200 in an anionic latex indicated more efficient crosslinking and faster curing into the matrix. This delivered improved chemical and stain resistances without compromising the hardness of the coating. Further, the use of less material also led to a lower VOC contribution: 70% less VOC for the ESO compared to the monomeric silane. These results might be extrapolated to a myriad of other applications in the coatings industry. In addition, the solvent-free ESO might be employed in solventborne or solventless formulations where monomeric epoxysilanes are already used.

Figure 7—Evolution of hardness of modified styrene acrylic coating.



Formulation based on : Styrene-acrylic emulsion
Silane rate : 1.2 wt% A-1871; 0.9 wt% MP 200
Formulation ageing : 7 days
Curing conditions : Oak panels – Spray drying – 130 g/m^2 – 7 days at RT
Koenig hardness : ISO 1522-1973

Surface Modifier for Metallic Particulates

In another approach to the evaluation of ESO into waterborne systems, we examined the ability of MP 200 to disperse metallic pigments in water. Paints and inks containing metal pigments are used in the paint and printing ink industries and are typically referred to as metallic paints and metallic inks. Applications in the paint industry include coating motor vehicles and other types of machinery. In the printing ink industry, these paints and inks are used to deliver unique printing effects and characteristics. In these applications, it is well known that these metallic pigments are very difficult to disperse in water due to the reaction between the metallic element and water. This reaction, which yields corrosion products such as metal oxides, generates a significant amount of hydrogen gas as a product. This phenomenon is called hydrogen gassing and can be accelerated in anionic latexes where the waterborne solution typically has an alkaline pH. Dispersion of the aluminum and/or zinc particulates is usually very difficult in these systems. As a result, three-component systems have been used that consist of the metallic pigment or particulate, the epoxy resin, and the amine curative or hardener. Alternatively, special additives may be used in the formulation to alleviate the hydrogen-gassing problem; however, they are typically expensive or difficult to formulate and may require other unique additives to enhance the effect.

We sought to overcome these issues around the dispersion of metallic pigments in water through the use of these new ESOs. Specifically, MP 200 was used to prepare a zinc-rich, two-component, waterborne epoxy primer typically used in protective coatings. As mentioned earlier, silanes have been used for modifying surfaces such as glass and metal. In this particular application, the intent was to modify the surface of the metallic particulates by reaction with the ESO and to inhibit the generation of hydrogen gas. The treated particulates could then be dispersed more readily in the formulation with less concern over hydrogen evolution in the container.

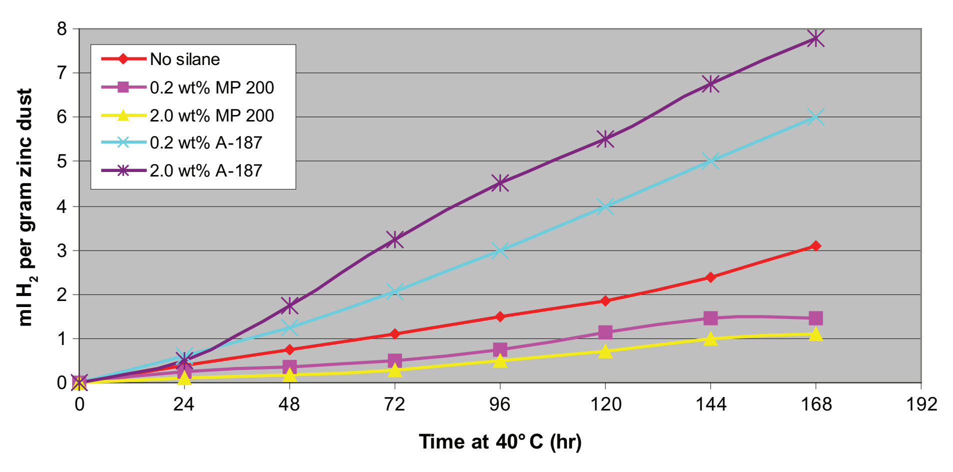


Figure 8—Hydrogen gassing behavior for each silane component using the hydrolyzate/metal dispersion procedure.

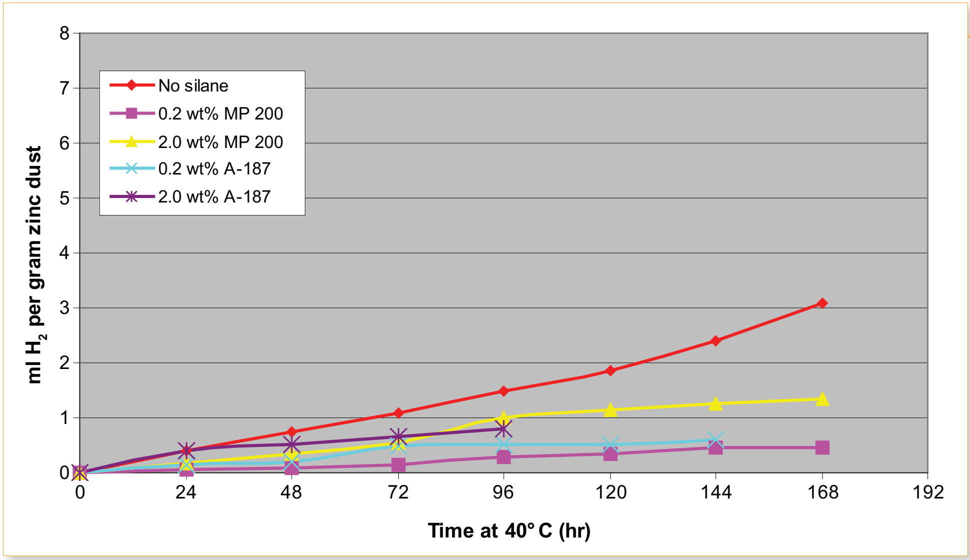


Figure 9—Hydrogen gassing behavior for each silane component using the hydrolyzate/binder dispersion procedure.

There are two methods for incorporating these silanes into the primer: (1) dispersion of the metallic component into a silane hydrolyzate, the resulting slurry or paste of which is dispersed into the binder, or (2) dispersion of the silane hydrolyzate into the binder followed by dispersion of the metallic particulates into the hydrolyzate/binder mixture. In both cases, the silane additives must be hydrolyzed to maximize reactivity for silane crosslinking. The general hydrolysis procedures for using both the ESO MP 200 and the monomeric A-187 are shown in the Methods and Materials section.

For each method, we examined the hydrogen gassing for the resulting formulation. In general, for the hydrolyzate/metal dispersions, the MP 200 hydrolyzate displayed a distinct reduction in hydrogen gassing relative to both the control sample (without silane) and the A-187 containing samples (*Figure* 8). Specifically, the higher loading of ESO gave better results; however, neither concentration gave a significant improvement. For the hydrolyzate/binder dispersions, the effect was clearly evident and both silane additives reduced hydrogen gassing to less than 2 mL after seven days (*Figure* 9). In addition, a lower level of silane additive is required to minimize the hydrogen gassing of the formulation relative to the hydrolyzate/metal dispersion procedure. Comparison of the two methods for the ESO MP 200 displayed a greater reduction for the hydrolyzate/binder dispersion procedure over the hydrolyzate/metal dispersion procedure. It is also noteworthy that the hydrolyzate/binder dispersion for the ESO MP 200 demonstrated more than six months of shelf stability whereas the A-187 based dispersions were shelf stable for approximately one week.

The stabilization of metallic particulates by the ESO may be very beneficial for applications where metallic effects and/or corrosion protection is required. ESOs have also been used for the dispersion of zinc dust for zinc-rich, waterborne basecoats or shop primers, and zinc and aluminum flakes for waterborne protective coatings. Monomeric epoxysilanes are currently used in corrosion protection applications in many sectors. We can foresee that ESOs can offer new alternatives to this very demanding industry, with incremental advantages given in terms of potential efficiency and VOC reduction.

SUMMARY

A new class of functional epoxysilanes has been introduced with great potential for a variety of applications in the coatings industry. These compounds are based on an oligomeric structure of an epoxysilane. The poly(epoxysiloxane) typically possesses lower alkoxy content and greater epoxy functionalization as compared to standard monomeric silanes. In testing, these features significantly reduced the VOC contribution of the material and improved the crosslinking efficiency within the resin matrix, respectively. Given that the material is 100% active as well, lower loadings are necessary for equivalent actives content and the material can be added neat or as a hydrolyzate to a waterborne formulation. The representative ESO—MP 200—demonstrated improved hydrogen gassing results as an additive in a metal-rich coating and primer formulation and improved stain resistance as an additive in a waterborne acrylic latex decorative paint formulation. These epoxysilane oligomers may be considered as a new technology platform to potentially overcome some of the challenges of the industry toward better quality products, higher cost effectiveness, and—equally or perhaps more important—products with lower impact on the environment. CT

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