Organosilane Technology in Coating Applications:
Review and Perspectives

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Abstract
Along with the continuous demand for improved performance, coating formulators are burdened with ever-tightening environmental protection regulations. The need to reduce VOCs, heavy metals like chromium VI and trialkyl tin, and other hazardous materials creates opportunities for the suppliers of high-performance, compliant material technologies. Ongoing research at universities and commercial organizations has demonstrated the effectiveness of organosilane technology – alone or in combination with other materials – to improve the performance of a variety of coating systems. Owing to the unique capability of organosilane molecules to form covalent bonding between inorganic and organic compounds along with the inherent stability and flexibility of the siloxane (Si-O-Si) bond, those molecules can provide multiple benefits in a broad range of coating systems. This paper will review the fundamentals of organosilane chemistry and its relevance to various coating applications, in particular the use of organosilanes in primers and their proven benefits for offering a healthier and more environmentally friendly alternative to chrome-based compounds in corrosion protection of metals. Using state-of-the-art analytical tools, recent experiments show the importance of the interphase design and control to optimize adhesion properties; viscoelastic properties; and scratch, abrasion and corrosion resistance. Organosilanes are key building blocks in the construction of this interphase and, as such, have the potential to impact the performance of the final composite. With the objective of controlling and optimizing interfacial properties, new technologies will be developed with resources aligned by Dow Corning to support the coating market. Specifically, the capabilities of the new Surface and Interface Solutions Center (SISC), established in May 2004, are presented.
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Introduction

Dow Corning pioneered the development of organosilane technology more than 50 years ago to provide new classes of materials with specific physical and chemical properties: silicones and silanes [1]. This research led to a new industry based on the synergy of organic and silicon chemistries.

The value of silane coupling agents was first discovered in the 1940s in conjunction with the development of fiberglass-reinforced polyester composites [2]. When initially fabricated, these composites were very strong, but their strength declined rapidly during aging. This weakening was caused by a loss of bond strength between the glass and resin. In seeking a solution, researchers found that organofunctional silanes – silicon chemicals that contain both organic and inorganic reactivity in the same molecule – functioned as coupling agents in the composites. A very small amount of an organofunctional alkoxysilane reacted at the glass-resin interface did not only significantly increase initial composite strength but also resulted in a dramatic retention of that strength over time.

Subsequently, other applications for silane coupling agents were discovered (e.g., mineral and filler treatment for composite reinforcement [3, 4]; adhesion of paints, inks and coatings [5, 6, 7]; reinforcement and crosslinking of plastics and rubber [8, 9, 10]; crosslinking and adhesion of sealants and adhesives [11, 12, 13, 14]; and in the development of water repellents and surface protection [15]).

Organosilane Chemistry

Monomeric silicon chemicals are known as silanes. A silane that contains at least one carbon-silicon bond (Si-C) structure is known as an organosilane.

The organosilane molecule (Figure 1) has three key elements:

- X – a non-hydrolyzable organic moiety. This moiety can be reactive toward another chemical (e.g., amino, epoxy, vinyl, methacrylate, sulfur) or non-reactive (e.g., alkyl).
- OR’ – a hydrolyzable group, like an alkoxy group (e.g., methoxy, ethoxy, isoproxy) or an acetoxy group that can react with various forms of hydroxyl groups present in mineral fillers or polymers and liberates alcohols (methanol, ethanol, propanol) or acid (acetic acid). These groups can provide the linkage with inorganic or organic substrates.
- R – a spacer, which can be either an aryl or alkyl chain, typically propyl-.

Through their dual reactivity, organosilanes serve as bridges between inorganic or organic substrates (such as minerals, fillers, metals and cellulose) and organic/polymeric matrices (such as rubber, thermoplastics or thermosets) and, hence, can dramatically improve adhesion between them. See Figure 2.

Typical Silane Applications

Coupling Agent: Organosilanes are used to couple organic polymers to inorganic materials. Typical of this application are reinforcements, such as fiberglass and mineral fillers, incorporated into plastics and rubbers.

![Figure 1. The organosilane molecule.](image1)

**Figure 1.** The organosilane molecule.

X-R-Si(OR’),

- X = Organic (e.g., Amino, Vinyl, Alkyl…)
- R’ = Methyl, Ethyl, Isopropyl…
- R = Aryl or Alkyl (CH₂)n with n = 0, 1 or 3

![Figure 2. How organosilane molecules work.](image2)

**Figure 2.** How organosilane molecules work.
**Adhesion Promoter:** Organosilanes are effective adhesion promoters when used as integral additives or primers for paints, inks, coatings, adhesives and sealants. As integral additives, they must migrate to the interface between the adhesive layer and the substrate to be effective. As a primer, the silane coupling agent is applied to the inorganic substrate before the product to be adhered is applied. By using the right organosilane, a poorly adhering paint, ink, coating, adhesive or sealant can be converted to a material that will frequently maintain adhesion even if subjected to severe environmental conditions (e.g., high temperature, underwater immersion or UV radiation).

**Dispersing/Hydrophobing Agent:** Organosilanes with hydrophobic organic groups attached to silicon will impart that same hydrophobic character to a hydrophilic inorganic surface. They are used as durable hydrophobing agents in concrete construction applications, including bridge and deck applications. They are also used to hydrophobize inorganic powders to make them free-flowing and dispersible in organic polymers and liquids. They also improve cure (by reducing catalyst inhibition) and electrical properties.

**Crosslinking Agent:** Organofunctional alkoxysilanes can react with organic polymers, resulting in a grafting of the trialkoxysilyl group onto the polymer backbone. The silane is then available to further react with moisture to crosslink the silane into a stable, three-dimensional siloxane structure. This mechanism can be used to crosslink polyethylene and other organic resins, such as acrylics and urethanes, to impart durability, water resistance and heat resistance to paints, coatings and adhesives.

**Typical Organosilanes**
A variety of organosilanes is available for use in coating applications (see Figures 3 and 4). Matching the organofunctional group on silicon with the resin polymer type to be bonded will dictate which silane coupling agent should be used in a particular application.

The organic group on the silane can be either nonreactive or reactive. Nonreactive silanes, such as those listed in Table I, are often used as dispersing or hydrophobing agents. They feature a nonreactive organic group (X), which is compatible with the matrix, and an alkoxy group (OR), which reacts with the substrate. Aminofunctional silanes, like those listed in Table II, are reactive at both ends and are useful in improving the adhesion of all kinds of coatings.

**Other Applications:** Organosilanes are also used as water scavengers in moisture-sensitive formulations, as blocking agents in antibiotic synthesis, polypropylene catalyst “donors” and as silicate stabilizers.

**Table III** lists other reactive organosilanes from Dow Corning that may be useful in a wide range of coating applications as well.
Table I. Nonreactive organosilanes from Dow Corning.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Organic Group</th>
<th>Alkoxy Group OR</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIAMETER® OFS-6070 Silane</td>
<td>Methyl</td>
<td>Methoxy</td>
<td>Methyltrimethoxysilane</td>
</tr>
<tr>
<td>Dow Corning® 1-6383 Silane</td>
<td>Methyl</td>
<td>Ethoxy</td>
<td>Methyltriethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6194 Silane</td>
<td>Methyl</td>
<td>Methoxy</td>
<td>Dimethyltrimethoxysilane</td>
</tr>
<tr>
<td>Dow Corning® Z-6265 Silane</td>
<td>Propyl</td>
<td>Methoxy</td>
<td>Propyltrimethoxysilane</td>
</tr>
<tr>
<td>Dow Corning® Z-6206 Silane</td>
<td>i-Butyl</td>
<td>Methoxy</td>
<td>Isobutyltrimethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6124 Silane</td>
<td>Phenyl</td>
<td>Methoxy</td>
<td>Phenyltrimethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6341 Silane</td>
<td>n-Octyl</td>
<td>Ethoxy</td>
<td>n-Octyltrimethoxysilane</td>
</tr>
</tbody>
</table>

Table II. Aminofunctional silanes from Dow Corning.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Organic Reactivity</th>
<th>Alkoxy Group OR</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow Corning® Z-6011 Silane</td>
<td>Amino</td>
<td>Ethoxy</td>
<td>Aminopropytriethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6020 Silane</td>
<td>Amino</td>
<td>Methoxy</td>
<td>Aminoethylaminopropytrimethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6094 Silane</td>
<td>Amino</td>
<td>Methoxy</td>
<td>Aminoethylaminopropytrimethoxysilane (high purity)</td>
</tr>
<tr>
<td>Dow Corning® Z-6137 Silane</td>
<td>Vinyl-benzyl-amino</td>
<td>Methoxy</td>
<td>Vinylbenzylated aminoethylaminopropytrimethoxysilane</td>
</tr>
<tr>
<td>Dow Corning® Z-6124 Silane</td>
<td>Vinyl-benzyl-amino</td>
<td>Methoxy</td>
<td>Low Cl version of XIAMETER® OFS-6032 Silane</td>
</tr>
<tr>
<td>Dow Corning® Z-6028 Silane</td>
<td>Benzylamino</td>
<td>Methoxy</td>
<td>Benzylated-aminoethylaminopropytrimethoxysilane</td>
</tr>
</tbody>
</table>

Table III. Additional reactive organosilanes from Dow Corning.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Organic Reactivity</th>
<th>Alkoxy Group OR</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIAMETER® OFS-6030 Silane</td>
<td>Methacrylate</td>
<td>Methoxy</td>
<td>γ-Methacryloxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6040 Silane</td>
<td>Epoxy</td>
<td>Methoxy</td>
<td>γ-Glycidoxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6076 Silane</td>
<td>Chloropropyl</td>
<td>Methoxy</td>
<td>γ-Chloropropytrimethoxysilane</td>
</tr>
<tr>
<td>Dow Corning® Z-6376 Silane</td>
<td>Vinyl</td>
<td>Methoxy</td>
<td>Vinyltrimethoxysilane</td>
</tr>
<tr>
<td>Dow Corning® Z-6300 Silane</td>
<td>Vinyl</td>
<td>Acetoxy</td>
<td>Vinylicacetoxy silane</td>
</tr>
<tr>
<td>Dow Corning® Z-6910 Silane</td>
<td>Mercapto</td>
<td>Ethoxy</td>
<td>Mercaptopropylthioxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6920 Silane</td>
<td>Disulfido</td>
<td>Ethoxy</td>
<td>Bis-(triethoxysilylpropyl)-disulfide</td>
</tr>
<tr>
<td>XIAMETER® OFS-6940 Silane</td>
<td>Tetrasulfido</td>
<td>Ethoxy</td>
<td>Bis-(triethoxysilylpropyl)-tetrasulfide</td>
</tr>
<tr>
<td>Dow Corning® Z-6675 Silane</td>
<td>Ureido</td>
<td>Methoxy</td>
<td>γ-Ureidopropytrimethoxysilane</td>
</tr>
<tr>
<td>XIAMETER® OFS-6106 Silane</td>
<td>Epoxy/melamine</td>
<td>Methoxy</td>
<td>Epoxy silane modified melamine resin</td>
</tr>
</tbody>
</table>

Key Reactions

Any application where organosilanes are involved requires the silane molecule to undergo hydrolysis and condensation reactions, which are illustrated in Figure 5.

Unlike the carbon-hydrogen (C-H) bond, the silicon hydride (Si-H) structure is reactive. It reacts with water to form reactive silanol (Si-OH) species. It can

Figure 5. The mechanism of hydrolysis, condensation and bonding of organosilanes to an inorganic surface.
also add across carbon-carbon double bonds to form carbon-silicon-based materials. The methoxy group on the carbon compound is stable as methyl ether, while its attachment to silicon gives a reactive and hydrolyzable methoxysilyl structure (Si-OCH₃). The potential impact of the organofunctional group on silicon atom reactivity depends on the distance between them. If the organic spacer group is a propylene linkage (e.g., -CH₂CH₂CH₂-) or longer, then the organic reactivity in the organofunctional silane will be similar to its organic analog.

Depending on the nature of the hydrolyzable groups attached to the silicon, we may distinguish the following categories of silanes: chlorosilanes, silazanes, alkoxysilanes and acyloxysilanes. Each exhibits unique chemical reactivity. These molecules will react with atmospheric moisture or water adsorbed on a surface to form silanols, while liberation of the corresponding by-product will occur (e.g., HCl, NH₃, alcohol or carboxylic acid). These silanols can then react with other silanols to form a stable siloxane bond (-Si-O-Si-). In the presence of hydroxyl groups at the surface of glass, minerals or metals (e.g., aluminum, steel), silanols will form a stable M–O-Si bond (M = Si, Al, Fe, etc.). This is the key chemistry that allows silanes to function as valuable surface-treating or “coupling” agents.

Because organosilanes hydrolyze before reacting with each other or with the hydroxyl groups present at a substrate surface, it is important to understand the reaction kinetics. The hydrolysis reaction can be catalyzed using either an acid or a base. Mechanisms of acid- and base-catalyzed hydrolysis of organosilanes have been extensively studied since their discovery [1, 16].

**Acid-catalyzed Hydrolysis:** Acid-catalyzed hydrolysis involves the protonation of the leaving OR group followed by a bimolecular Sₙ₂-type displacement of the leaving group by water. See Figure 6.

**Base-catalyzed Hydrolysis:** Base-catalyzed hydrolysis involves attack on silicon by a hydroxyl ion to form a pentacoordinate intermediate followed by bimolecular displacement of alkoxo by hydroxyl. Any high-electron acceptors group next to the Si atom will dramatically increase hydrolysis under basic pH. See Figure 7.

**Hydrolysis Rate:** The rate of hydrolysis by both mechanisms is influenced by the nature of the organic group on silicon as well as the leaving alkoxo group. Another factor is pH. As pH changes, so does the hydrolysis rate. This is true for both acid- and base-catalyzed reactions.

As soon as alkoxo groups begin hydrolyzing, condensation to high-molecular-weight species may occur.

**The Hydrolysis/Condensation Balance:** The rates of both hydrolysis and condensation are influenced by changing pH levels. This is true whether the reaction is catalyzed by acid or base. However, the optimum pH for hydrolysis is not optimum for condensation. Finding the best balance between hydrolysis and condensation is one of the keys to the successful utilization of organosilane chemistry for a specific application (Figure 8).

**Interface Design and Materials Science**

Interface design and materials science deal with surfaces, but “surface” is a concept with many definitions. Surfaces can range from large, easily visible forms, such as plastic sheets, metal
panels, glass panes, skin, wood or concrete; to fibers, fillers and pigments; and ultimately to particulate and microscopic forms such as 10⁻⁹m size sol-gel nanoparticles.

Organosilanes can be linked to these surfaces in a number of ways. Theoretically, a monolithic layer is sufficient to provide benefit. In practice, however, to ensure uniform coverage, more than one layer of silane is usually applied to a surface. This results in a tight siloxane polymeric network close to the inorganic surface that diffuses into subsequent overlays. The coupling to the organic matrix can be complex. The reactivity of a thermoset polymer should be matched to the reactivity of the silane. For example, an epoxysilane or aminosilane will bond to an epoxy resin; an aminosilane will bond to a phenolic resin; and a methacrylate silane will bond through styrene cross-linking to an unsaturated polyester resin.

Figure 9 illustrates how covalent bonding forms between a silane and a metal surface.

Bonding through a silane coupling agent is, however, often more complex than a single bond. At the interface, the silane reacts with itself and also with the polymer, crosslinking and interlocking mechanically with the polymer in a way that is difficult to separate. Inter-diffusion phenomenon and semi-inter-penetrating network (IPN) phenomena occur in the interphase region and are critical to the overall composite performance (Figure 10) [17, 18]. The key factors that control the formation of this network are the hydrolysis/condensation rate, the solubility parameters, structural characteristics of the two materials and their thermal stability [19]. Even with thermoset polymers, where reactivity plays an important role, chemical structure matching will enhance the physical properties of the composite.
A third way to look at how organosilanes bond with a surface is through the material reinforcement modality. Fillers treated with a silane coupling agent employ coupling agent/polymer chain bonding to create an interphase zone with specific properties. A plasticized transition zone is created between the hard, glassy filler and the soft, elastic matrix. See Figure 11.

A fourth approach, which moves beyond the creation of an interphase to the realm of particle formation is the sol-gel process (Figure 12). In this process, water is added to a silane molecule, generating silicon oxide, which is a solid particle. The product of elimination is alcohol. By controlling the hydrolysis and condensation conditions, including pH, the presence or absence of salts, and time, it is possible to affect the morphology and, depending on the route taken, to create either sols (solid suspensions) or three-dimensional gel networks.

Through the addition of templating agents, it is also possible to organize the particles and self-assemble them into pre-functionalized nanobuilding blocks.

With sol-gel technology, it is possible to synthesize and design materials and interfaces under very mild conditions and achieve nanoparticle synthesis that imparts transparency, low weight, hardness and functionality to coatings. See Figure 13.

### Silane Technology in Paints and Coatings

Tightening volatile organic compound (VOC) content regulations and increasing health and environmental concerns about the use of heavy metals (e.g., chrome, lead, cadmium, mercury, zinc, cobalt, etc.) in the coatings industry, along with demand for improved physical properties and extended performance life, have spurred interest in silane technology.
The unique capability to create covalent bonds between inorganic and organic compounds and the inherent stability of the siloxane (Si-O-Si) bond make this technology a key component in high-performance paints and coatings. These properties lie at the heart of the ability of these materials to withstand physical, chemical, weather and thermal degradation. Therefore, the use of organosilanes in coatings has provided improvements in minerals dispersion; water, chemical, abrasion and UV resistance; adhesion; and flow properties.

Paint and coating applications that can benefit from silane technology include primers, heat-resistant coatings, industrial maintenance coatings, hygienic coatings, marine biofouling control, abrasion-resistant coatings, automotive clearcoats and architectural coatings.

**Primers**

A segment of the coatings industry in which silanes provide crucial functionality is primer systems, in which silanes are used either to pretreat a substrate or are added into a coating formulation as an adhesion promoter. Alkoxysilanes have, therefore, broad utility in formulating primers and coatings for a variety of metallic and siliceous substrates. Especially attractive to the formulator is the wide range of organoreactive and non-reactive moieties attached to the silicon atom (Tables I-III), which allows formulas to be tailored to specific application performance requirements. Widely known as adhesion promoters, organosilane primers also offer controlled hydrophobicity, excellent UV and thermal stability, surface activity, chemical resistance, and hence, corrosion protection.

One example of the use of organosilane technology to create high-performance primers is the use of zinc-rich primers for the galvanic protection of ferrous substrates. Hydrolyzates of tetra-ethoxy silane (TEOS) are combined with zinc metal powder. Transesterification of the alkyl orthosilicate has been found to improve solution stability [20]. (Reference the Dow Corning brochure, *A Guide to Silane Solutions from Dow Corning*, page 20.)

Amino- and epoxy-functional silanes improve adhesion to siliceous and metallic substrates. Figure 14 illustrates the superior adhesion durability of primers formulated with an epoxy-functional silane over the adhesion of other primer technologies in use today with aluminum substrates.

**Paints and Coatings**

Siloxane-alkyd, siloxane-epoxy and siloxane-acrylic chemistries can be used to improve industrial, architectural and marine antifouling coatings. By combining silanes with organic resins and through careful manipulation of the hydrolysis/condensation balance, it is possible to create coatings with superior properties, such as low viscosity, high solids content and low VOC; adhesion to metals, cements and quartz-like surfaces; low combustibility; and improved heat and UV resistance, which results in improved gloss retention. Figure 15 illustrates the improvement in gloss retention that can be achieved through the use of organosilane technology.
Impregnation
In masonry treatment applications, isobutyl, n-octyl and iso-octyl silanes can be used to control wetting and reduce water uptake (Figure 16).

Additionally, phenyl and fluorinated silanes can be used to improve substrate resistance to chemicals, including detergents and disinfectants, by creating a hydrophobic surface that is comparable to the lotus-leaf effect found in nature (Figure 17).

Abrasion-Resistant Coatings
Coatings employing sol-gel technology can be developed to improve the abrasion resistance of plastic lenses in glasses. Silica is highly resistant to abrasion, and sol-gel technology enables the creation of particles so small that they are virtually invisible, making it ideal for this application. Figure 18 illustrates the significant improvement in scratch and abrasion resistance that can be achieved through the use of sol-gel coating formulations.

New Perspectives
Today, organosilane chemistry is enabling the development of new, more environmentally responsible technologies for corrosion protection and the creation of “smart” surfaces that are easy to clean. It is also enabling paint and coating formulators to meet the challenges involved in switching from solvent-based to water-based coatings in their drive to comply with increasingly stringent VOC regulations.

Metal Corrosion Protection
Differences in the metal/coating coefficient of thermal expansion (CTE) can lead to thermal stresses resulting in micro-cracks and allow water and electrolytes to access the metal, which, in turn, leads to debonding of the coating.

Figure 16. Masonry impregnation.

Figure 17. The lotus-leaf effect.

Figure 18. Abrasion resistance performance comparison (sol-gel).

Creating a silane interpenetrating network between the metal substrate and the organic coating layers provides:

- Barrier properties that are resistant to contaminants and electrolytes, due to the high crosslinking density,
- Resistance to water ingress along the interface due to the innate hydrophobicity of bis(triethoxysilyl)ethane (BTSE), sulfido and other silanes,
- Adhesion to the metal surface, resulting from the coupling effect between the silane and the surface metal-hydroxyls, e.g., γ-glycidoxypropyltrialkoxysilane (GPS) or γ-aminopropyltrialkoxysilane (APTS),
- Enhanced stress dissipation upon weathering cycling conditions, due to low Tg inclusions,
- And the opportunity to replace chrome, if the silane is combined with an appropriate/non-toxic corrosion inhibitor.

BSTE silanes have demonstrated a superior capability to γ-aminopropyltriethoxysilane (APTES) to create barrier properties. As seen in Figure 19, with BTSE, there is a huge increase of polarization resistance after cure (i.e., pinhole-free film formation).

**Chromium Replacement**

State-of-the-art metal surface preparations for adhesive bonding consist mainly of anodization or etching processes that employ strong acids. Many of these surface preparations also contain hexavalent chromium (CrVI). The surface treatment is followed by the application of a corrosion-inhibiting adhesive primer containing high levels of VOCs and chromium salts. Since the early 1980s, issues related to hazardous waste disposal, preservation of the environment, and potential impact on employee health and safety have driven the industry to seek alternatives to chromium [21, 22].

In the early 1980s, it was found that a primer composed of an acrylic copolymer, an epoxy resin, a silica sol and a trialkoxysilane compound provided superior paintability and grease and corrosion resistance after paint coating [23]. Twelve years later, it was found that a wash primer, without the acrylic copolymer or the epoxy resin, could provide similar benefits [24]. Metal was pretreated with an alkaline solution containing at least one of a dissolved inorganic silicate and a dissolved inorganic aluminolate, an organofunctional silane and a crosslinking agent containing trialkoxysilyl groups. The metal was then dried to completely cure the functional silane to form an insoluble primer layer bonded tightly to the metal substrate. Combining the cure profiles and barrier properties of organic resins with the thermal and UV stability of silanes, formulators have created high-performance coatings with excellent resistance to corrosion and chemical attack as well as thermal and UV degradation (see Figure 14).

A blend of an epoxy resin, a curing agent for epoxy resins, an organofunctional alkoxysilane and a catalyst for condensation polymerization of a silane compound was found to provide high heat resistance and excellent mechanical strength [25]. Similarly, complete or partial hydrolysis of alkyl/phenyl alkoxysilanes to form silanol or alkoxy functional siloxane resins and the subsequent reaction with epoxy resins have been shown to produce copolymers with improved water and moisture resistance [26]. Utilizing the functional groups available from silane monomers, resin formulators have created organo-functional (e.g., epoxy and amine) silicone resins for epoxy resin modification [27, 28, 29].

The benefits of different silane blends were explored further by several groups. Lapique et al. [30] and Van Ooij et al. [31] have shown that BTSE bonds to aluminum and decreases the hydrolysis and/or corrosion rate at the adhesive-metal interface due to its hydrophobic character, while APTES only increases the initial adhesive bond strength – hence the benefit of combining the two. Combinations of bis(trimethoxysilyl)propylamine and bis[triethoxysilylpropyl]tetrasulfide in the appropriate ratio were found useful to achieve both optimal film formation and protection against rapid
electrolyte diffusion to aluminum or hot-dip galvanized steel [31], thanks to the right balance between hydrophobicity and adhesive bonding at the metal-coating interface. J. Vereecken et al. [32] studied the morphology of the films as a function of the film-forming parameters (e.g., silane types and concentration, rate of hydrolysis and condensation reaction, processing time, and degree of hydration of the metals prior to coating). They concluded that as the permeability of the silane film decreases, its impedance increases proportionally, hence improving the passivation of the metals studied (aluminum, galvanized steel). Watts et al. [33, 34] showed that growth of aluminum oxide occurs when γ-glycidoxypropyltrimethoxysilane (GPS) is cured on polished aluminum sheet at elevated temperature, creating an Al/O/Si interphase. These works showed that bonding performances of adhesives can be maintained or improved when aluminum is treated with GPS silane versus conventional chromic or phosphoric acid anodization (see Figure 14). As an alternative to a silanization process in solution, Boeiro et al. [35, 36] recently demonstrated the effectiveness of vapor-phase, or low-pressure plasma silanization to treat aluminum alloy. This approach provides an effective way to address problems such as uncontrolled hydrolysis and polycondensation reactions, and solvent elimination.

Examples based on the sol-gel process can also be found in the literature [37, 38]. The approach consists in forming Al₂O₃ or SiO₂ protective layers at the metal surface by using silane-based materials (TEOS, BTSE, APTES, GPS). This mild chemical treatment, followed by a sintering process, is an alternative to more aggressive classical treatments.

**“Smart” Surfaces**

Another emerging application for organosilane chemistry is the development of “smart” surfaces – surfaces that are uncharacteristically hydrophobic or hydrophilic, hydrophobic and oleophobic (a state that can be obtained through the use of fluorosilane and sol-gel technologies), or exhibit the lotus-leaf effect (a hydrophobic micro-roughness).

Figure 20 illustrates the use of octamethylocyclooctasiloxane (OMCTS) and an atmospheric glow discharge process to create a hydrophobic treatment for cotton fabric that results in a super-hydrophobic surface with easy cleaning/water repellence properties. Figure 21 illustrates how tetramethylocyclooctasiloxane (TMCTS) can be used to create a hydrophilic effect on PET and PP, which are naturally hydrophobic. The SiOₓ deposition makes the surface fully wettable. Enhanced barrier to oxygen performance is demonstrated as well. Note how the hydrophilic “Q” and “T” Si species levels have been manipulated to achieve surface hydrophilicity, compared with the levels exhibited in the hydrophobicity example (Figure 20).
**Water-Based Systems**

The desire for water-based coating formulations is on the rise, both for their ease of use and their ability to help formulators meet environmental regulations (low VOC).

Solutions include the use of:

- A silane-derived acrylic polyol emulsion
- Pre-hydrolyzed and pre-condensed silanes including specifically designed catalyst systems
- Replacement of methoxy/ethoxy with other, nontoxic leaving groups, such as OH, glycol or heavy alcohols

These solutions may be applied to the formulation of water-based construction material treatments as well as water-based paints.

There are two challenges inherent to the use of water-based formulations: 1) wetting of low-surface-energy substrates and 2) maintaining reactivity/shelf-life balance. However, through the use of organosilane chemistry, it is possible to create water-based systems that outperform conventional solvent-based systems.

Figure 22 illustrates the development of a silane-derived acrylic polyol emulsion, a three-step process. First, an acrylic polyol is pre-reacted with an alkoxy-functional silane intermediate. Hydrolysis is catalyzed under alkaline conditions. Finally, condensation of silanols with acrylic polyol results in a crosslinked acrylic siloxane.

**Figure 22. Creation of a silane-derived acrylic polyol emulsion.**

![Image of silane-derived acrylic polyol emulsion]

**Practical Considerations for Water-Based Formulations**

A primary concern for water-based formulations is the stability of alkoxy-silanes [39]. If alkoxy silane adhesion promoters react with water, how can they be used in water-based coatings formulations? For silanes to provide the expected benefits of adhesion or crosslinking, the hydrolysis reaction is a necessary and desired step in the process [1]. Modifying the silane, via transesterification, from methoxy functionality to longer alkoxy groups (e.g., isopropoxy) can slow down the hydrolysis process without preventing it. While accepting the inevitability of hydrolysis and subsequent condensation of alkoxy silanes, coating formulators have reversed this apparent limitation by utilizing organosilane chemistry to improve the performance of many water-based coatings.

Coatings fail as a result of water absorption into the film, ultimately reaching the coating-substrate interface. Because of the specific organic-inorganic character of organosilanes, they can enhance the adhesion of coatings to metal or siliceous substrates by forming covalent bonds, and hence increasing the density of linkages between the a coating and the substrate. Furthermore, by selecting the proper combination of organosilanes, the hydrophobicity of the interphase can be improved, which will contribute to hydrolytic stability upon service-life.

Addition of alkoxy silanes to a coating formulation can create a more tightly crosslinked, hydrophobic film much less susceptible to moisture attack [1]. Additions of 0.5% silane (based on system solids) into acrylic latex-based coatings provide significant benefit.

Treatment of mineral pigments and fillers (e.g., silica, titanium dioxide, etc.) with alkoxy silanes is well known in the coatings industry. While pigment or filler suppliers can offer pre-treated particles and aggregates, similar benefits can be observed by incorporating the alkoxy silane directly into a water-based coating formulation (in-situ treatment). The presence of water at high pH results in hydrolysis of the silane and condensation around the solid particles. The net effect is improved dispersion, more...
complete incorporation of the inorganic particle into the binder matrix and improved physical properties. However, successful use of silanes in water-based formulations requires good dispersion of the silane prior to complete hydrolysis and condensation. Appropriate mixing is essential. Along with good stirring, pre-diluting the silane into coalescing solvent or plasticizer before adding it to the latex will minimize condensation between the silane monomers (and potential gel formation) and will favor interaction with the other components of the coating formulation.

**Future Trends**

**Environmental**

Environmental concerns will increase. For example, European regulations and the recent introduction of REACH will accelerate the development and the commercial use of alternative anti-corrosion treatments to replace chromium VI in plating, coil coating and metal painting. Organosilanes have proven their ability to improve durability under extreme operating conditions through the formation of strong, covalently bonded IPNs between metal surfaces (aluminum, steel) and coatings, adhesives or sealants and, as such, may provide a viable solution.

**Sol-gel Processes**

Although known and studied for several decades, sol-gel processes are not widely used at an industrial level for coatings purposes. However, the recent evolution of the organosilanes market may open the door to accurately designed materials created under mild conditions. Some self-cleaning, easy-to-clean and scratch-resistant coating applications are already using sol-gel technology.

**“Smart” Surfaces**

Several groups of researchers are developing templating surface concepts designed to control wettability [40, 41], tailoring cell adhesion or designing molecular gradients for controlled materials assembly and directed transportation on surfaces. Other properties, such as anti-scratch, anti-graffiti, lotus-leaf effect, brilliance and refractive index, are also being developed using silane-based chemistry and technologies.

**The Dow Corning Surface and Interface Solutions Center**

To continue its leadership position in the development of silane technology, Dow Corning has recently invested in a new R&D facility: the Surface and Interface Solutions Center (SISC). The center’s expertise is articulated around surface and interface science and applications for Si-containing chemicals. More specifically, the SISC is developing materials science core competencies around fillers, reinforcement and adhesion. It also has several “application cells” focusing on target markets and products such as Plastics and Rubber, Coatings, and Adhesives and Sealants. These cells are equipped with state-of-the-art equipment and facilities. The center is staffed by experienced PhD-level researchers and engineers from a variety of horizons and is connected to Dow Corning’s global network of internal and external experts. The core group is located in Europe; however, team members are also conducting work in the United States and Asia.

The SISC is a market-driven organization designed to optimize the benefits and values of silicon-based chemistry and thereby create value for Dow Corning customers. Its mission is to discover and develop unique surface, interface and interphase technologies and solutions. The center develops and concentrates knowledge and databases on surface and interface sciences as they apply to Dow Corning’s target markets and products. It cooperates closely with customers, technical partners and others in Dow Corning’s global organization to provide appropriate solutions, including new molecules, composites and/or processes. The center works to identify unmet customer and market needs that can be met by Dow Corning’s extensive materials science and synthesis capabilities.

**Conclusion**

Organosilane chemistry brings a wide variety of benefits to coatings, including:

- Adhesion to “difficult” substrates
- Strong bonding to hydrophilic reactive sites (through covalent bonding and the creation of interpenetrating networks)
- Low moisture uptake (hydrophobicity balance)
- Thermal stability
- UV resistance
- Low surface tension
- Controlled Tg inclusions, resulting in stress reduction or increased surface hardness
- Reduced dirt pick-up and anti-graffiti properties (hydrophobicity/oleophobicity)

Dow Corning continues to pioneer the development of innovative technologies and applications for organosilane and silicon-containing materials through our global research team and the Surface and Interface Solutions Center (SISC). From automotive to marine to aerospace, from electronics to building construction to sporting goods, Dow Corning silanes are an important component of today’s advanced materials technologies. They enable a wide range of new materials, including coatings, to be developed with greater reliability and improved performance.
References

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