

BACK TO BASICS

A Silane Primer: Chemistry and Applications of Alkoxy Silanes

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Formulators in the paint, ink, adhesives, water repellents, and other related industries require materials that resist peeling and penetration in spite of prolonged exposure to heat, cold, moisture, and chemical attack. Research into these problems resulted in the development of alkoxy functional silanes for use as adhesion promoters, crosslinkers, and hydrophobes. The intent of this paper is to briefly review the unique chemistry of this class of materials and to discuss three areas of product development that have benefited from the utilization of silanes: surface treatment, additive, and reactive intermediate. This discussion will include recommendations for specific organic/silane combinations.

INTRODUCTION

The ability of silane added to a coating formulation to migrate to the substrate interface and improve bonding is well known. In addition, silanes have been added to latices and hydrolyzed to form an interpenetrating polymer network (IPN) polymer with improved properties.¹ Two types of alkoxy silanes have widespread application in the coatings industries: alkyl/aryl and organofunctional.

Possessing both organic and inorganic properties, these hybrid chemicals react with the polymer and mineral components, forming durable covalent bonds across the interface. It has been proposed that these bonds are hydrolyzable, but can reform, and therefore provide a means of stress relaxation at the organic/inorganic interface. The results are improved adhesion and durability.²

CHEMISTRY OF ORGANOFUNCTIONAL ALKOXYSILANES

The general formula of an alkoxy silane shows two classes of moieties attached to the silicon atom:



R is a nonhydrolyzable organic moiety that can be either an alkyl, aromatic, organofunctional, or a combination of any of these groups. These groups provide the organic compatibility which allows the silane to form IPNs, or in the case of reactive organofunctional silanes, to co-react with the coating polymer. Alkyl and aryl silanes are utilized to improve gloss, hiding power, mixing time, and other properties related to improved pigment dispersion. Alkyl and aryl silanes are also utilized to provide hydrophobic surfaces in applications such as water repellents.

The X represents alkoxy moieties, most typically methoxy or ethoxy, which react with the various forms of hydroxyl groups and liberate methanol or ethanol. These groups can provide the linkage with inorganic substrates, pigment, or filler to improve coating integrity and adhesion. The methoxy groups are also capable of reacting with hydroxy functional polymers.

Reaction of these silanes involves four steps (see *Figure 1*). Initially, hydrolysis of the alkoxy (X) groups occurs. It is after the first and second alkoxy groups are hydrolyzed that condensation to oligomers follows. Compared to the hydrogen of a carbinol moiety, the silanol hydrogen is more electrophilic and much more reactive. This is due to the larger, more electropositive, atomic structure of silicon which results in a high dipole moment for the silanol group and greater hydrogen bonding. The tendency toward self condensation can be controlled by using fresh solutions, alcoholic solvents, dilution, and by careful selection of pH ranges.

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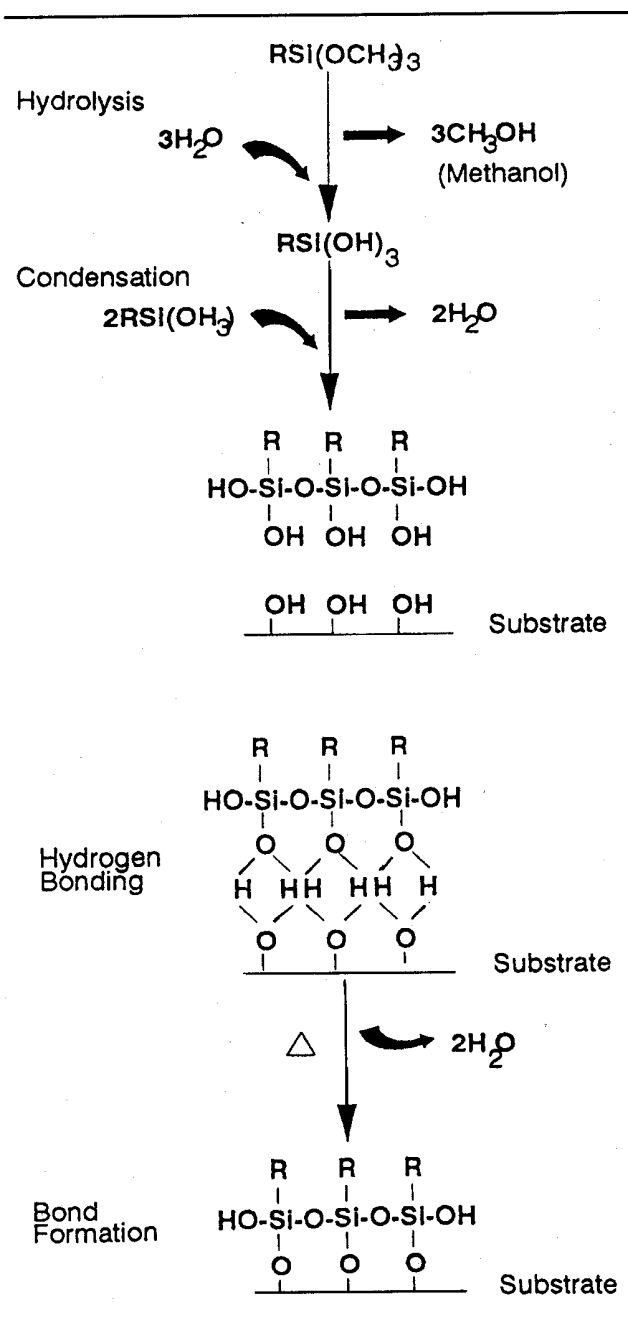


Figure 1—Reaction process of alkoxy silanes

Silanetriols are most stable at pH 3-6, but condense rapidly at pH 7-9.³

The third methoxy group upon hydrolysis is oriented towards, and hydrogen bonds with, hydroxy sites on the substrate. Finally, during drying or curing, a covalent bond is formed with the substrate and water is liberated. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. A moderate cure cycle (110°C/15 min) will leave silanol groups remaining in free form and, along with any silane organofunctionality, may bond with the subsequent topcoat, forming an IPN and providing improved adhesion.⁴

UTILIZATION OF ORGANOFUNCTIONAL ALKOXY SILANES

There are three basic methods of utilizing silanes in a coatings application: (1) surface treatment, which includes particle (i.e., pigments and fillers) treatment formulated into primers, and water repellents; (2) additive into paints, inks, and adhesives; and (3) reactive intermediate for silicone resin synthesis and organic resin modification. Each of these methods requires special consideration.

SURFACE TREATMENT

Often the silane is subjected to hydrolysis prior to the surface treatment. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Less stable bonds are formed with oxides of boron, iron, and carbon. Alkali metal oxides and carbonate do not form stable bonds with Si-O. Sufficient water for hydrolysis may be available from atmospheric moisture, or on the substrate surface. In some cases, it may be necessary to add water to increase the degree of hydrolysis.

The most straightforward method of silylating a surface with a silane is from an alcohol solution. A two percent silane solution can be prepared in the alcohol of choice (methanol, ethanol, and isopropanol are typical choices). The solution can be wiped, dipped, or sprayed onto the surface. When dipping a large object, e.g., glass plates, allow one to two minutes of submersion to allow silane migration to the surface. After the surface dries, excess material can be gently wiped, or briefly (alcohol) rinsed off. Particles, e.g., pigments and fillers, can be silylated by stirring them in a solution for two to three minutes and then decanting the solution. The particles can then be rinsed with alcohol. Cure of the silane layer is for 5-10 min at 110°C or for 24 hr at ambient conditions.

Flow and adhesion are improved by applying silanes from aqueous alcohol solutions.³ A 95% ethanol-5% water solution is adjusted to pH 4.5-5.5 with acetic acid. Silane is added with stirring to yield a 2-10% final concentration.

Table 1—Recommendations for Water Soluble and Hydrophilic Polymers

Water Soluble & Hydrophilic Polymers	Silane			
	A	B	C	D
Acrylic latex	—	—	—	✓
Cellulosic	—	—	—	✓
Heparin	—	—	—	✓
Polyhydroxyethylmethacrylate	—	—	—	✓
Polysaccharide	—	—	—	✓
Polyvinyl alcohol	✓	—	✓	—
Polyvinyl acetate	—	—	✓	—
EVA	—	✓	—	—

(a) N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.

(b) 3-Methacryloxypropyltrimethoxysilane.

(c) N-[2(vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane.

(d) 3-Glycidoxypropyltrimethoxysilane.

Table 2—Recommendations for Thermoset Systems

Thermoset Systems	Silane			
	A	B	C	D
Diallylphthalate	✓	✓	✓	—
Epoxy	✓	—	✓	✓
Furan	✓	—	—	✓
Imide	✓	—	✓	—
Melamine	✓	—	—	✓
Paralene	—	—	✓	—
Phenolic	✓	—	✓	✓
Polyester	—	✓	✓	—
Urethane	✓	—	—	✓

(a) N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.
 (b) 3-Methacryloxypropyltrimethoxysilane.
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 (d) 3-Glycidoxypropyltrimethoxysilane.

Typically, six hours are given to allow for hydrolysis and silanol formation.

Low VOC aqueous solutions can be prepared by dissolving 0.5-2.0% of the silane in pH adjusted (4.5-5.5 pH with acetic acid) water. For less soluble silanes, 0.1% of a nonionic surfactant could be added and an emulsion rather than a solution is prepared. Stability of aqueous silane solutions varies from hours for the alkyl silanes to weeks for the aminosilanes. Poor solubility parameters limit the use of long chain alkyl and aromatic silanes by this method.

Filler and pigment treatment is usually accomplished by a spray-on method. It assumes that the sufficient hydroxyl moieties are present on the filler to allow reaction with the silane. The silane is prepared as a 25% solution in alcohol. The powder is placed in a high intensity solid mixer, the solution is pumped into the agitated powder as a fine spray, then the powder is dried.

ADDITIVE

The additive method is another means of utilizing alkoxy silanes. Here the silane becomes a component of the coating from which it diffuses or migrates to the inorganic substrate and reacts. Silanes, as additives, are generally effective in concentrations ranging from 0.05 to 1.00% of the coating.⁵ Effective coupling action with silanes as additives depends on meeting several criteria:

(1) Good mechanical dispersion of the silane into the coating will assure uniform coupling and best efficiency.

(2) The solubility parameters and reactivities of the polymer and silane must be compatible. No reaction should occur in storage. Matched solubility is necessary for silane interpenetration into the polymer.⁶ Proper pH ranges must be maintained to avoid silane condensation.

(3) Silanes, as additives in filled systems, in storage will migrate to the inorganic surfaces of pigments and fillers. Some excess silane should be added for that which is adsorbed onto the mineral surface of the fillers and for the silane which fails to migrate through the polymer to the coating/substrate interface.

(4) Hydrolysis to silanetriol by water must occur to render the silane active for coupling. Proper moisture conditioning of filler or addition of extra water will help assure that the silane hydrolyzes and couples.

Table 3—Recommendations for Thermoplastic Systems

Thermoplastic Systems	Silane			
	A	B	C	D
Acrylic	✓	✓	—	✓
ABS	—	—	✓	—
Alkyd	—	✓	✓	✓
Cellulosics	✓	—	—	—
Nylon	✓	—	—	—
Nitrile rubber	✓	—	—	—
PEEK	—	—	✓	—
Polyamide	✓	—	✓	—
Polycarbonate	✓	—	—	✓
Polyethylene	—	—	✓	—
Polyphenylene oxide	—	—	✓	—
Polyphenylene sulfide	✓	—	✓	—
Polypropylene	—	—	✓	—
Polystyrene	—	✓	✓	✓
Polysulfone	✓	—	—	—
Polyvinylbutyral	✓	—	—	—
Polyvinyl chloride	✓	—	—	✓

(a) N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.
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 (c) N-[2(vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane.
 (d) 3-Glycidoxypropyltrimethoxysilane.

REACTIVE INTERMEDIATE

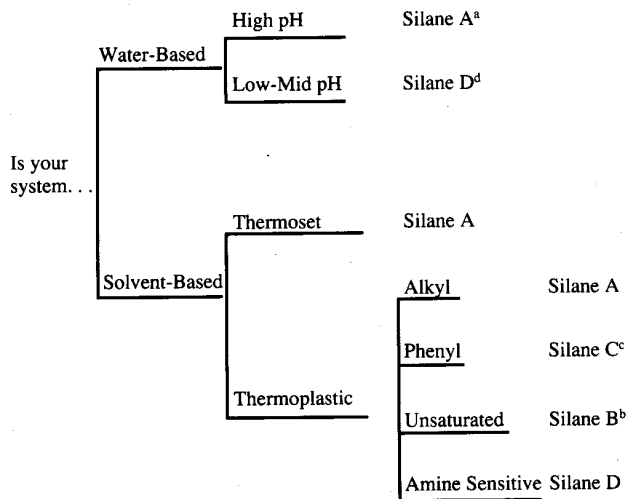
Alkoxy silanes, when cold blended with acrylic emulsions, undergo emulsion polymerization and siliconize the acrylic emulsion particles. These silicone acrylic emulsions have been shown to have improved weathering characteristics.¹ Silicone modification of acrylic latex coatings is applicable to both air-dry and baking systems.

Silicone modification is accomplished by adding the silanes dropwise to the acrylic latex (pH 8.0-9.0), and the mixture is stirred for three to five minutes to solubilize the silane. The latex is then allowed to stand for 8-16 hr to allow the silane to polymerize. The emulsion polymerization reaction is a two-step process. The first step is the hydrolysis of the alkoxy groups; the second step is the silanol condensation to form siloxane bonds. The silanol groups also react with hydroxy groups on the latex particle to form a silicone organic copolymer.

By utilizing a unique blend of methoxy silanes, a silicone-modified latex was formulated into a high gloss, heat-cured coating designed for maintenance applications using conventional latex methods. This coating was exposed in Florida (45° South) for 48 months. As little as 10% silicone modification improved the gloss retention and color retention with no effect on checking, chalking, and dirt retention.

High Gloss Light Blue Water-Based Maintenance Paint Cured at 60 sec/550°F

% Silane	60° Gloss				Delta E Color Change				
	0	1	2	4	1	2	3	4	
0	64	60	38	25	8	1.4	1.9	4.2	4.1
10	69	61	48	41	28	2.6	3.2	3.1	4.0
20	85	78	65	56	52	1.8	2.1	1.8	3.7
30	84	74	64	60	53	2.0	2.1	1.6	2.4

Table 4—General Silane Selection

(a) N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.

(b) 3-Methacryloxypropyltrimethoxysilane.

(c) N-[2(vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane.

(d) 3-Glycidoxypropyltrimethoxysilane.

Another approach to utilizing alkoxy silanes that deserves study is the synthesis of novel silicone resinous polymers by hydrolysis of silane blends in slightly acidic solution. Low VOC materials can be produced by balancing the composition linearity, the degree of hydrolysis, and the removal of the methanol produced during hydrolysis. The resulting polymers are often compatible with organic polymers and can be cold blended to form interpenetrating networks. Materials of this type may be utilized in paints, primers, inks, and adhesives where excellent adhesion, weathering resistance, and high temperature stability are required.

RECOMMENDATIONS

Selection of the appropriate silane is accomplished by empirical evaluation of silanes within the recommended groups. Exact prediction of the optimum silane for a specific system is extremely difficult. Silane performance is affected by several factors – surface energy, wet out, absorption, adsorption, acid-base interaction, interpenetrating network formation, and covalent reaction. Key

consideration must be given to the polymer/silane reactivity, compatibility, and the polymer/silane solubility parameters.

Tables 1-3 list recommendations for water-based or hydrophilic, thermoset, and thermoplastic polymers. While these lists are not all-inclusive, several generalizations can be drawn from the data.

Despite the wide selection of silane chemistries available, and the fact that a specific coating system can benefit from more than one of these chemistries, silanes A, B, and C are chosen more often than any others (see Table 4). As an example: for coating systems which are water-based, hydrophilic, or amine sensitive, silane D is a viable selection for screening.

Solvent-based, high solids, solventless, or powder systems, whether they are thermoset or thermoplastic, will benefit from the utilization of an aminosilane. While silane A does have excellent water solubility, allowing for low VOC application, the need for greater hydrophobicity or higher temperature stability would suggest the use of silane C.

CONCLUSION

Owing to the highly reactive methoxy sites, organic compatibility, and unique silicone chemistry, alkoxy silanes provide the coating formulator with a myriad of straightforward synthesis solutions to high performance application requirements.

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