

W W W . U N I T E D C H E M . C O M



SILANE COUPLING AGENT GUIDE



SILICONES



SILANES



CATALYSTS



COATINGS

SPECIALTIES

SILANE COUPLING AGENT CHEMISTRY

The general formula of an organosilane shows two classes of functionality.



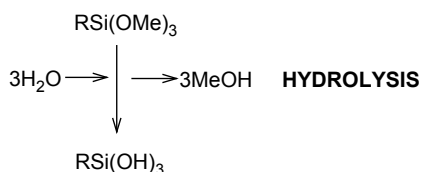
The X functional group is involved in the reaction with the inorganic substrate. The bond between X and the silicon atom in coupling agents is replaced by a bond between the inorganic substrate and the silicon atom. X is a hydrolyzable group, typically, alkoxy, acyloxy, amine, or chlorine. The most common alkoxy groups are methoxy and ethoxy, which give methanol and ethanol as byproducts during coupling reactions. Since chlorosilanes generate hydrogen chloride as a byproduct during coupling reactions, they are generally utilized less than alkoxy silanes.

R is a nonhydrolyzable organic radical that possesses a functionality which enables the coupling agent to bond with organic resins and polymers. Most of the widely used organosilanes have one organic substituent.

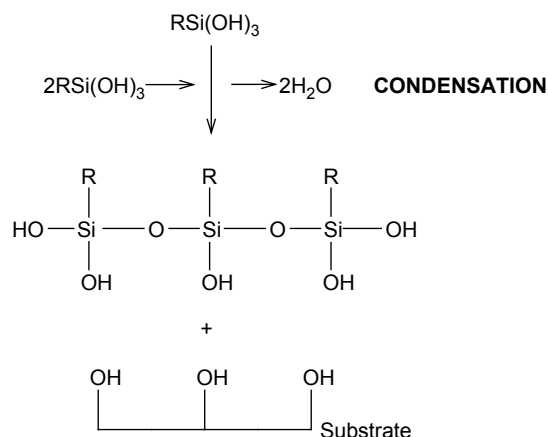
In most cases the silane is subjected to hydrolysis prior to the surface treatment. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. Stable condensation products are 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 carbonates do not form stable bonds with Si – O –.

Water for hydrolysis may come from several sources. It may be added, it may be present on the substrate surface or it may come from the atmosphere. Water for hydrolysis may also be generated in situ by dissolving chlorosilanes in excess alcohol. Reaction with alcohol produces alkoxy silanes and HCl, which can react with additional alcohol to form an alkyl halide and water.

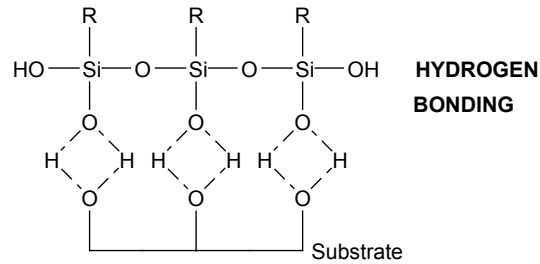
Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile X groups attached to silicon occurs.



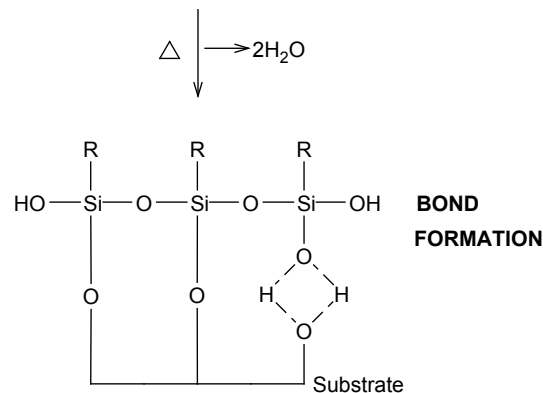
Condensation to oligomers follows.



The oligomers then hydrogen bond with OH groups of the substrate.



Finally during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. The two remaining silanol groups are present either bonded to other coupling agent silicon atoms or in free form.



The number of reactive sites on a surface area and the type of silane deposition sought, i.e. monolayer, multilayer or bulk, are all factors which can be used in calculating the amount of silane necessary to silylate a surface. In order to provide monolayer coverage, the concentration of reactive sites (silanols) should be determined. Most siliceous substrates have 4 – 12 silanols per μm^2 . Thus, one mole of evenly distributed silane should cover an average of 7500 m^2 . The oligimerization of silanes with multiple groups thwarts the capability of computing stoichiometries, but order of magnitude computations are successful. Silanes with one hydrolyzable group can be utilized to produce surfaces with monolayers of consistent stoichiometry. These materials are more expensive and produce surfaces with less hydrolytic stability. The number of silanols on a surface is varied by thermal history. In one example, a siliceous surface having 5.3 silanols per μm^2 had only 2.6 after exposure to 400°C and less than one after exposure to 850°C . Higher concentrations of silanol groups may be produced by treating material with warm hydrochloric acid. Silanol anions may be produced by treating the surfaces with alkaline detergent or, more radically, by treatment with methanolic potassium hydroxide. Optimum deposition of silanes with more than one hydrolyzable group is often defined as the amount necessary to produce a surface of uniform energy. A value defined as the wetting surface (ws) describes the area in m^2 one gram of silane deposited from solution will cover. In combination with data on the surface area of a siliceous substrate in m^2/g the amount of silane required for deposition may be calculated. Most composite, adhesive, and coating formulations do not follow any stoichiometry, but simply define optimal concentration by operation success. For most fillers, a treatment level of 0.02 – 1.00% by weight is used.

Selecting a Silane Coupling Agent

Selection of the appropriate coupling agent is accomplished by empirical evaluation of silanes within predicted categories. Exact prediction of the best silane is extremely difficult. Increased bond strength by utilization of silanes is a result of a complex set of factors – wet out, surface energy, boundary layer absorption, polar adsorption, acid-base interaction, interpenetrating network formation and covalent reaction. Strategies for optimization must take into account the materials on both sides of the interface and their susceptibilities to the various coupling factors. Generally speaking the initial approach is to select a single coupling agent and assume a direct bond between the two materials. The most common application for silane coupling agents is to bond an inorganic substrate to a polymer.

Inorganic-Si-R-Organic

The number of hydrolyzable X groups on the silane is another important parameter in controlling bond characteristics. The traditional silane coupling agents contain three hydrolyzable groups. They have maximum hydrolytic stability but tend to be hydroscopic. At the opposite end are the silanes with one hydrolyzable group. These yield the most hydrophobic interfaces but have the least long term hydrolytic stability. Silanes with two hydrolyzable groups form less rigid interfaces than silanes with three hydrolyzable groups. They are often used as coupling agents for elastomers and low modulus thermoplastics. Polymeric silanes with recurrent trialkoxy or dialkoxysilanes offer better film-forming and primer capabilities. For enhanced hydrolytic stability or economic benefit, non-functional silanes such as short chain alkyltrialkoxysilanes or phenyltrialkoxysilanes can be combined in ratios up to 3:1 with functional silanes.

In more difficult bonding situations, mixed silanes or silane network polymers may be employed. These include inorganic to inorganic or organic to organic. In these cases, reaction of the silanes with themselves is critical.

Organic-O-Si-R-R-Si-O-Organic

An example of mixed silane application is the use of mixtures of epoxy and amine functional silanes to bond glass plates together. A more general use is bonding organic to organic. Primers, prepared by pre-hydrolyzing silanes to resins in order to form bulk layers on metal substrates, are examples of the application of silanes as network polymers.

Thermal Stability

Most silanes have moderate thermal stability, making them suitable for plastics that process below 350°C or have continuous temperature exposures below 150°C. Silanes with an aromatic nucleus have higher thermal stability. A relative ranking where Z is the functional groups is as follows:

Class	Example	Thermal Limit
ZCH ₂ CH ₂ SiX ₃	N/A	< 150°C
ZCH ₂ CH ₂ CH ₂ SiX ₃	A0700	390°C
ZCH ₂ AromaticCH ₂ CH ₂ SiX ₃	T2902	495°C
Aromatic SiX ₃	P0320	550°C

COUPLING AGENT SELECTION GUIDE

Table 1 - Thermosets		
Name	Silane Class	UCT Product
diallylphthalate	amine	A0700 A0750
	styryl	S1590
epoxy	amine	A0700 A0750 T2910
	epoxy	G6720 E6250
	chloroalkyl	C3300
	mercapto	M8450 M8500
imide	chloromethylaromatic	T2902
	amine	A0700 A0750 T2910
melamine	amine	A0700 A0750 T2910
	epoxy	G6720 E6250
	alkanolamine	B2408
paralene	chloromethylaromatic	T2902
phenolic	amine	A0700 A0750 T2910
	chloroalkyl	C3300
	epoxy	G6720 E6250
photoresist, negative	silazane	H7300 D6208
	vinyl	D6208
	aromatic	P0320
photoresist, positive	silazane	H7300
	aromatic	P0320
	phosphine	D6110
polyester	amine	A0700 A0750 T2910
	methacrylate	M8550
	styryl	S1590
	vinyl	V4917 V4910
urethane	amine	A0700 A0750 T2910
	alkanolamine	B2408
	epoxy	G6720 E6250
	isocyanate	I7840

Table 2 - Thermoplastics

Name	Silane Class	UCT Product
cellulosics	amine	A0700 A0750 T2910
	isocyanate	I7840
polyacetal	thiouronium	S1590
polyacrylate	methacrylate	M8550
	ureido	T2507
polyamide (nylon)	amine	A0700 A0750 T2910 A0742 PS076
	ureido	T2507
polyamide-imide	chloromethylaromatic	T2902
	amine	A0700 A0750 A0800
polybutylene terephthalate	amine	A0750
	isocyanate	I7840
polycarbonate	amine	A0700 A0750 T2910
polyetherketone	amine	A0750 A0800
ethylene-vinyl acetate copolymer	ureido	T2507
polyethylene	amine	A0700 A0742 A0750
	vinyl	V4910 V4917
	styryl	S1590
polyphenylene oxide	amine	A0700 A0750 T2910
	aromatic	P0320
polyphenylene sulfide	amine	A0700 A0750 T2910
	mercapto	M8450 M8500 B2494
	chloromethylaromatic	T2902
polypropylene	aromatic	P0320 P0330
	styryl	S1590
polystyrene	aromatic	P0320 P0330
	epoxy	G6720 E6250
	vinyl	V4910 V4917
polysulfone	amine	A0700 A0750 T2910
polyvinyl butyral	amine	A0700 A0742 A0750
polyvinyl chloride	amine	A0700 A0750 T2910
	alkanolamine	B2408

Table 3 - Sealants

Name	Silane Class	UCT Product
acrylic	acrylic	M8550
	styryl	S1590
	epoxy	G6720 E6250
polysulfides	mercapto	B2494 M8500 M8450
	amine	A0699 A0700 A0742 A0750 T2910

Table 4 - Rubbers

Name	Silane Class	UCT Product
butyl	epoxide	G6720 E6250
neoprene	mercapto	M8450 M8500
isoprene	mercapto	M8450 M8500
fluorocarbon	styryl	S1590
epichlorohydrin	amine	A0699 A0700 A0742 A0750
	mercapto	M8450 M8500
silicone	amine	A0700 A0750
	allyl	A0567

Table 5 - Water Soluble and Hydrophilic Polymers

Name	Silane Class	UCT Product
cellulosic	epoxy	G6710 G6720
	isocyanate	I7840
heparin	amine	A0800 PS076
	epoxy	G6710 G6720
	isocyanate	I7840
polyethylene oxide	isocyanate	I7840
polyhydroxyethylmethacrylate	epoxy	G6710 G6720
	isocyanate	I7840
polysaccharide	epoxy	G6710 G6720
	isocyanate	I7840
polyvinyl alcohol	epoxy	G6710 G6720
	isocyanate	I7840
siliceous	all listed in Table 1	A0700
aluminum, zirconium, tin and titanium metals	all listed in Table 1, but the epoxies, acrylates and quats preferred	S1590 M8540
copper, iron	polyamine	T2910 PS076
	phosphine	D6110
gold, precious metals	phosphine	D6110
	mercapto	B2494 M8500
silicon	vinyl	D6208

SILANE REFERENCE LIST

Alkanoamine

B2408 Bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane

Allyl

A0567 Allyltrimethoxysilane

Amine

A0699 N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane

A0700 N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane

A0742 3-Aminopropylmethyldiethoxysilane

A0750 3-Aminopropyltriethoxysilane

A0800 3-Aminopropyltrimethoxysilane

PS076 (N-Trimethoxysilylpropyl)polyethyleneimine

T2910 Trimethoxysilylpropyldiethylenetriamine

Aromatic

P0320 Phenyltriethoxysilane

P0330 Phenyltrimethoxysilane

Chloroalkyl

C3300 3-Chloropropyltrimethoxysilane

Chloromethylaromatic

T2902 1-Trimethoxysilyl-2(p,m-chloromethyl)phenylethane

Epoxy

E6250 2-(3,4-Epoxycyclohexyl)ethyltrimethoxysilane

G6720 3-Glycidoxypropyltrimethoxysilane

Isocyanate

I7840 Isocyanatopropyltriethoxysilane

Mercapto

B2494 Bis[3-(triethoxysilyl)propyl]tetrasulfide

M8450 3-Mercaptopropylmethyldimethoxysilane

M8500 3-Mercaptopropyltrimethoxysilane

Methacrylate

M8550 3-Methacryloxypropyltrimethoxysilane

Phosphine

D6110 2-(Diphenylphosphino)ethyltriethoxysilane

Silazane

D6208 1,3-Divinyltetramethyldisilazane

H7300 Hexamethyldisilazane

Styryl

S1590 3-(N-Styrylmethyl-2-aminoethylamino)propyltrimethoxysilane hydrochloride

Ureido

T2507 N-(Triethoxysilylpropyl)urea

Vinyl

D6208 1,3-Divinyltetramethyldisilazane

V4910 Vinyltriethoxysilane

V4917 Vinyltrimethoxysilane

APPLYING A SILANE COUPLING AGENT

Deposition from aqueous alcohol solutions is the most facile method for preparing silylated surfaces. 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% final concentration. Five minutes should be allowed for hydrolysis and silanol formation. Large objects, e.g. glass plates, are dipped into the solution, agitated gently, and removed after 1 – 2 minutes. They are rinsed free of excess materials by dipping briefly in ethanol. Particles, e.g. fillers and supports, are silylated by stirring them in solution for 2 – 3 minutes and then decanting the solution. The particles are usually rinsed twice briefly with ethanol. Cure of the silane layer is for 5 – 10 minutes at 110°C or for 24 hours at room temperature (<60% relative humidity).

For aminofunctional silanes such as A0700 and A0750 this procedure is modified by omitting the additional acetic acid. The procedure is not acceptable for chlorosilanes as bulk polymerization often occurs. Silane concentration of 2% is a starting point. It usually results in deposition of trialkoxysilanes as 3 – 8 molecular layers. Monoalkoxysilanes are always deposited in monolayers or incomplete monolayers. Caution must be exercised if oven curing. Exhausted, explosion-proof ovens should always be used.

Deposition from aqueous solutions is employed for most commercial fiberglass systems. The alkoxy silane is dissolved at 0.5 – 2.0% concentration in water. For less soluble silanes, 0.1% of a non-ionic surfactant is added prior to the silane and an emulsion rather than a solution is prepared. If the silane does not contain an amine group, the solution is adjusted to pH 5.5 with acetic acid. The solution is either sprayed onto the substrate or employed as a dip bath. Cure is at 110 – 120°C for 20 – 30 minutes.

Stability of aqueous silane solutions varies from hours for the simple alkyl silanes to weeks for the aminosilanes. Poor solubility parameters limit the use of long chain alkyl and aromatic silanes by this method. Distilled water is not necessary, but water containing fluoride ions must be avoided.

Bulk deposition onto powders, e.g. filler treatment, is usually accomplished by a spray-on method. It assumes that the total amount of silane necessary is known and that sufficient adsorbed moisture is present on the filler to cause hydrolysis of the silane. The silane is prepared as a 25% solution in alcohol. The powder is placed in a high intensity solid mixer, e.g. twin cone mixer with intensifier. The solution is pumped into the agitated powder as a fine spray. In general, this operation is completed within 20 minutes. Dynamic drying methods are most effective. If the filler is dried in trays, care must be taken to avoid wicking or skinning of the top layer of treated material by adjusting heat and air flow.

Integral blend methods are used in composite formulations. In this method the silane is used as a simple additive. Composites can be prepared by the addition of alkoxy silanes or silazanes to dry-blends of polymer and filler prior to compounding. Generally 0.2 – 1.0 weight percent of silane (on the total mix) is dispersed by spraying the silane in an alcohol carrier onto a pre-blend. The addition of the silane to non-dispersed filler is not desirable in this technique since it can lead to agglomeration. The mix is dry-blended briefly and then melt compounded. Vacuum devolatilization of byproducts of silane reaction during melt compounding is necessary to achieve optimum properties. Properties are sometimes enhanced by adding 0.5 – 1.0% of tetrabutyl titanate or benzyl dimethylamine to the silane prior to dispersal. Amino-functional silanes are available in concentrate form for dry-blending with nylons and polyesters. Concentrates eliminate any need for solvent dispersion and devolatilization and reduce variability due to relative humidity and shelf-aging.

Deposition as a primer is employed where a bulk phase is required as a transition between a substrate and a final coating. The silane is dissolved at 50% concentration in alcohol. One to three molar equivalents of water are added. The mixture is allowed to equilibrate for 15 – 20 minutes and then diluted to 10% concentration with a higher boiling polar solvent. Materials to be coated with the primer are dipped or sprayed and then cured at 110 – 120°C for 30 – 45 minutes.

Chlorosilanes such as V4900 may be deposited from alcohol solution. Anhydrous alcohols, particularly ethanol or isopropanol are preferred. The chlorosilane is added to the alcohol to yield a 2 – 5% solution. The chlorosilane reacts with the alcohol producing an alkoxy silane and HCl. Progress of the reaction is observed by halt of HCl evolution. Mild warming of the solution (30 – 40°C) promotes completion of the reaction. Part of the HCl reacts with the alcohol to produce small quantities of alkyl halide and water. The water causes formation of silanols from alkoxy silanes. The silanols condense with those on the substrate. Treated substrates are cured for 5 – 10 minutes at 110°C or allowed to stand 24 hours at room temperature.

Chlorosilanes and silylamines may also be employed to treat substrates under aprotic conditions. Toluene, tetrahydrofuran or hydrocarbon solutions are prepared containing 5% silane. The mixture is refluxed for 12 – 24 hours with the substrate to be treated. It is washed with the solvent. The solvent is then removed by air or explosion-proof oven drying. No further cure is necessary. This reaction involves a direct nucleophilic displacement of the silane chlorines by the surface silanol. If monolayer deposition is desired, substrates should be pre-dried at 150°C for 4 hours. Bulk deposition results if adsorbed water is present on the substrate. This method is cumbersome for large scale preparations and rigorous controls must be established to ensure reproducible results. More reproducible coverage is obtained with monochlorosilanes.

Silazanes such as H7300 and D6208 may be used as treatments in concentrated form or as 10 – 20% solutions in aprotic solvents. In some applications, parts are exposed for 5 – 10 minutes by dipping or in microelectronics by spin-on techniques. Optimum reactivity is at 30 – 50°C. An alternate method of treatment is to expose parts to 50°C vapor for 2 – 6 hours. Ammonia is the byproduct of silazane reaction and areas should be ventilated.

Appendix

Calculations of necessary silane to obtain minimum uniform multilayer coverage can be obtained knowing the values of the wetting surface of silane (ws) and the surface area of filler.

$$\text{Amount of filler (g)} = \frac{(\text{amount of filler}) \times (\text{surface area of filler})}{\text{wetting surface (ws)}}$$

Relative surface area of common fillers m²/g:

E-Glass	0.1 – 0.12
Silica, ground	1 – 2
Kaolin	7
Clay	7
Talc	7
Si, diatomaceous	1 – 3.5
Calcium silicate	2.6

NOTES

GENERAL INFORMATION

PRICES AND TERMS

Our prices are subject to change without notice. The price in effect when we receive your order will apply. All prices are in US Dollars and are F.O.B. Bristol, PA 19007. Terms of payment are net 30 days.

MINIMUM ORDERS

We welcome all orders, therefore, we do not have a minimum order requirement. When ordering, please include your purchase order number, complete "Ship To" and "Bill To" address, catalog number, quantity, and description of product(s). Also include your name and a phone number where you can be reached should we have any questions concerning your order.

SHIPMENTS

Normal process is shipment within one business day after receipt of an order if material is in stock. Unless special shipping arrangements are made, all orders will be sent via Federal Express Ground. Shipping and handling charges (freight, insurance, hazardous materials fee) will be added to the invoice unless requested by the customer.

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We offer special pricing for volume purchases and standing orders. Please call a sales representative for more information on special pricing qualifications.

RETURN POLICY

Our sales staff will process your return. Before returning merchandise, please call to obtain a return authorization number from a sales representative. We will need to know the reason for the return, date of purchase, purchase order number, invoice number, catalog number and lot number of product returned in order to issue a return authorization number.

WARRANTY

All products manufactured by UCT Specialties, LLC are guaranteed against defects in materials or workmanship for a period of 90 days from shipment. UCT Specialties, LLC will replace any items that prove to be defective during that time period.

The exclusive remedy requires the end user to first advise UCT Specialties, LLC of the defective product by phone or in writing. Secondly, the defective product must be returned within 30 days after proper approval from the Product Manager. All returns must indicate the purchase order number, lot number and the shipping date. UCT Specialties, LLC total liability is limited to the replacement cost of UCT products.

This warranty does not apply to damage resulting from misuse.

Placing An Order

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