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Hydrophobicity, Hydrophilicity and Silane Surface Modification



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Nanoparticle Synthesis



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Front Cover Photos: Water rolls off a duck's back. Lotus leaves exhibit superhydrophobicity. Biological systems are dependent on water, but at the same time must control the interaction. In a sense, all living organisms exhibit behaviors that can be described as both hydrophobic and hydrophilic.

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Gelest **Hydrophobicity, Hydrophilicity and Silane Surface Modification**

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Hydrophobicity, Hydrophilicity and Silane Surface Modification

by Barry Arkles

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Silanes and Surface Modification

Silanes are silicon chemicals that possess a hydrolytically sensitive center that can react with inorganic substrates such as glass to form stable covalent bonds and possess an organic substitution that alters the physical interactions of treated substrates.



organic substitution allows permanent property modification

hydrolyzeable alkoxy (alcohol) groups

Property modifications include:

- Hydrophobicity
- Release
- Dielectric
- Absorption
- Orientation
- Hydrophilicity
- Charge Conduction

Applications include:

- Architectural Coatings
- Water-Repellents
- Anti-stiction Coatings for MEMs
- Mineral Surface Treatments
- Fillers for Composites
- Pigment Dispersants
- Dielectric Coatings
- Anti-fog Coatings
- Release Coatings
- Optical (LCD) Coatings
- Bonded Phases
- Self-Assembled Monolayers (SAMs)
- Crosslinkers for Silicones
- Nanoparticle Synthesis

In contrast with silanes utilized as coupling agents in adhesive applications, silanes used to modify the surface energy or wettability of substrates under normal conditions do not impart chemical reactivity to the substrate. They are often referred to as non-functional silanes. The main classes of silanes utilized to effect surface energy modification without imparting reactivity are:

Hydrophobic Silanes

- Methyl
- Linear Alkyl
- Branched Alkyl
- Fluorinated Alkyl
- Aryl
- Dipodal

Hydrophilic Silanes

- Polar
- Hydroxylic
- Ionic
- Charge inducible /charge switchable
- Embedded Hydrophilicity
- Masked

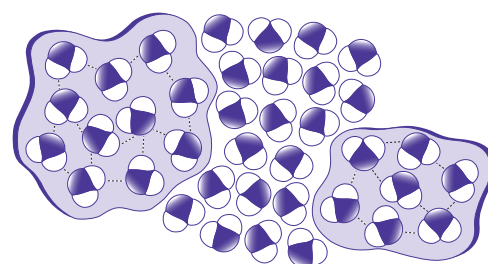
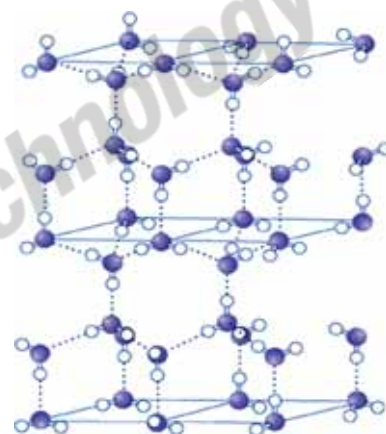
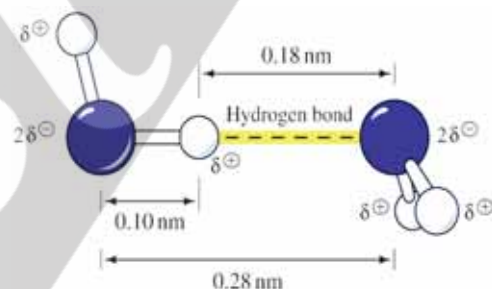
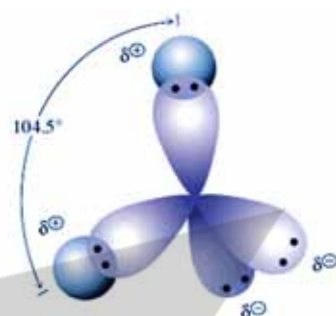
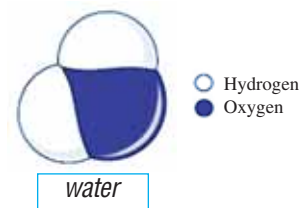
Water, Hydrophobicity and Hydrophilicity

Hydrophobic and **Hydrophilic** are frequently used descriptors of surfaces. A surface is hydrophobic if it tends *not to* adsorb water or be wetted by water. A surface is hydrophilic if it tends *to* adsorb water or be wetted by water. More particularly, the terms describe the interaction of the boundary layer of a solid phase with liquid or vapor water. Silanes can be used to modify the interaction of boundary layers of solids with water with a high degree of control, effecting variable degrees of hydrophobicity or hydrophilicity.

Since the interaction of water with surfaces is frequently used to define surface properties, a brief review of its structure and properties can be helpful. Although the structure of water is a subject of early discussion in the study of physical sciences, it is interesting to note that the structure of liquid water is still not solved and, even so, most technologists lose appreciation of what is known about its structure and properties.

The quantum calculation of the structure of an isolated H₂O molecule has evolved to the currently accepted model which demonstrates a strong dipole, but no lone electron pairs associated with sp³ hybridized orbitals of oxygen. This model of isolated H₂O conforms most closely to the vapor state and extrapolation often leads to the conclusion that water is a collection of individual molecules which associate with each other primarily through dipole interactions. The polar nature of water, with its partial positive and partial negative dipole, explains why bulk water readily dissolves many ionic species and interacts with ionic surfaces. The difference between isolated vapor phase water and bulk liquid water is much more extreme than can be accounted for by a model relying only on dipole interaction. The properties of bulk liquid water are strongly influenced by hydrogen bond interactions. In the liquid state, in spite of 80% of the electrons being concerned with bonding, the three atoms of a water molecule do not stay together as discrete molecules. The hydrogen atoms are constantly exchanging between water molecules in a protonation-deprotonation process. Both acids and bases catalyze hydrogen exchange and, even when at its slowest rate of exchange (at pH 7), the average residence time of a hydrogen atom is only about a millisecond. In the liquid state, water molecules are bound to each other by an average of three hydrogen bonds. Hydrogen bonds arise when a hydrogen that is covalently bound to an oxygen in one molecule of water nears another oxygen from another water molecule. The electrophilic oxygen atom “pulls” the hydrogen closer to itself. The end result is that the hydrogen is now shared (unequally) between the oxygen to which it is covalently bound and the electrophilic oxygen to which it is attracted (O-H...O). Each hydrogen bond has an average energy of 20 kJ/mol. This is much less than an O-H covalent bond, which is 460 kJ/mol. Even though an individual hydrogen bond is relatively weak, the large number of hydrogen bonds that exist in water which pull the molecules together have a significant role in giving water its special bulk properties. In ice, water molecules are highly organized with four hydrogen bonds. Liquid water is thought to be a combination of domains of molecules with 3-4 hydrogen bonds separated by domains with 2-3 hydrogen bonds, subject to constant turnover - the *flickering cluster model*.

This brief description of water is provided in order to give the insight that whenever a solid surface interacts with bulk water it is interacting with a soft matter structure, not simply a collection of individual molecules. Surface interactions with water must compete with a variety of internal interactions of liquid phase water: van der Waals forces, dipole interactions, hydrogen bonding and proton exchange.



Wettability and Contact Angle

A surface is said to be wetted if a liquid spreads over the surface evenly without the formation of droplets. When the liquid is water and it spreads over the surface without the formation of droplets, the surface is said to be hydrophilic. In terms of energetics, this implies that the forces associated with the interaction of water with the surface are greater than the cohesive forces associated with bulk liquid water. Water droplets form on hydrophobic surfaces, implying that cohesive forces associated with bulk water are greater than the forces associated with the interaction of water with the surface. Practically, hydrophobicity and hydrophilicity are relative terms. A simple quantitative method for defining the relative degree of interaction of a liquid with a solid surface is the contact angle of a liquid droplet on a solid substrate. If the contact angle of water is less than 30°, the surface is designated hydrophilic since the forces of interaction between water and the surface nearly equal the cohesive forces of bulk water and water does not cleanly drain from the surface. If water spreads over a surface and the contact angle at the spreading front edge of the water is less than 10°, the surface is often designated as superhydrophilic provided that the surface is not absorbing the water, dissolving in the water or reacting with the water. On a hydrophobic surface, water forms distinct droplets. As the hydrophobicity increases, the contact angle of the droplets with the surface increases. Surfaces with contact angles greater than 90° are designated as hydrophobic. The theoretical maximum contact angle for water on a smooth surface is 120°. Micro-textured or micro-patterned surfaces with hydrophobic asperities can exhibit apparent contact angles exceeding 150° and are associated with superhydrophobicity and the “lotus effect”.



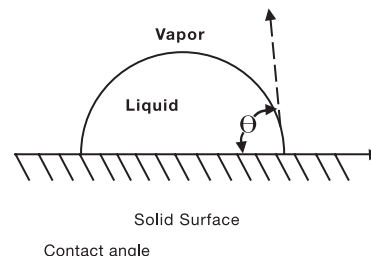
Ordinary Surface-
“typical wetting”

Hydrophobic-
“poor wetting”



Hydrophilic-
“good wetting”

Contact Angle Defines Wettability



Contact Angle of Water on Smooth Surfaces

| | θ |
|--|----------|
| heptadecafluorodecyltrimethoxysilane* | 115° |
| poly(tetrafluoroethylene) | 108-112° |
| poly(propylene) | 108° |
| octadecyldimethylchlorosilane* | 110° |
| octadecyltrichlorosilane* | 102-109° |
| tris(trimethylsiloxy)-silylethyldimethylchlorosilane | 104° |
| octyldimethylchlorosilane* | 104° |
| dimethyldichlorosilane* | 95-105° |
| butyldimethylchlorosilane* | 100° |
| trimethylchlorosilane* | 90-100° |
| poly(ethylene) | 88-103° |
| poly(styrene) | 94° |
| poly(chlorotrifluoroethylene) | 90° |
| human skin | 75-90° |
| diamond | 87° |
| graphite | 86° |
| silicon (etched) | 86-88° |
| talc | 50-55° |
| chitosan | 80-81° |
| steel | 70-75° |
| methacryloxypropyltrimethoxysilane | 70° |
| gold, typical (see gold, clean) | 66° |
| intestinal mucosa | 50-60° |
| glycidoxypropyltrimethoxysilane* | 49° |
| kaolin | 42-46° |
| platinum | 40° |
| silicon nitride | 28-30° |
| silver iodide | 17° |
| soda-lime glass | <15° |
| gold, clean | <10° |

* Note: Contact angles for silanes refer to smooth treated surfaces.

Critical Surface Tension and Adhesion

While the contact angle of water on a substrate is a good indicator of the relative hydrophobicity or hydrophilicity of a substrate, it is not a good indicator for the wettability of the substrate by other liquids. Critical surface tension is associated with the wettability or release properties of a solid. It serves as a better predictor of the behavior of a solid with a range of liquids.

Liquids with a surface tension below the critical surface tension (γ_c) of a substrate will wet the surface, i.e., show a contact angle of 0 ($\cos\theta_e = 1$). The critical surface tension is unique for any solid and is determined by plotting the cosine of the contact angles of liquids of different surface tensions and extrapolating to 1. The contact angle is given by Young's equation:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cdot \cos\theta_e$$

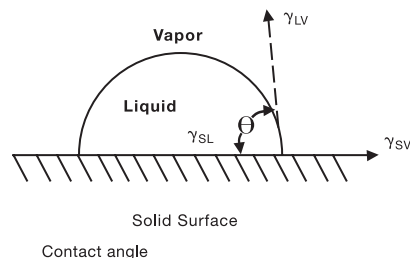
where γ_{sl} = interfacial surface tension, γ_{lv} = surface tension of liquid.

Hydrophilic behavior is generally observed by surfaces with critical surface tensions greater than 45 dynes/cm. As the critical surface tension increases, the expected decrease in contact angle is accompanied with stronger adsorptive behavior and with increased exotherms associated with the adsorption.

Hydrophobic behavior is generally observed by surfaces with critical surface tensions less than 35 dynes/cm. At first, the decrease in critical surface tension is associated with oleophilic behavior, i.e. the wetting of the surfaces by hydrocarbon oils. As the critical surface tensions decrease below 20 dynes/cm, the surfaces resist wetting by hydrocarbon oils and are considered oleophobic as well as hydrophobic.

Silane treatment has allowed control of thixotropic activity of silica and clays in paint and coating applications. In the reinforcement of thermosets and thermoplastics with glass fibers, one approach for optimizing reinforcement is to match the critical surface tension of the silylated glass surface to the surface tension of the polymer in its melt or uncured condition. This has been most helpful in resins with no obvious functionality such as polyethylene and polystyrene. Immobilization of cellular organelles, including mitochondria, chloroplasts, and microsomes, has been effected by treating silica with alkylsilanes of C₈ or greater substitution.

Contact Angle Defines Wettability



Contact angle

Critical surface tensions

| | γ_c dynes/cm |
|--|------------------------|
| heptadecafluorodecyltrichlorosilane | 12.0 |
| poly(tetrafluoroethylene) | 18.5 |
| octadecyltrichlorosilane | 20-24 |
| methyltrimethoxysilane | 22.5 |
| nonafluorohexyltrimethoxysilane | 23.0 |
| vinyltriethoxysilane | 25 |
| paraffin wax | 25.5 |
| ethyltrimethoxysilane | 27.0 |
| propyltrimethoxysilane | 28.5 |
| glass, soda-lime (wet) | 30.0 |
| poly(chlorotrifluoroethylene) | 31.0 |
| poly(propylene) | 31.0 |
| poly(propylene oxide) | 32 |
| polyethylene | 33.0 |
| trifluoropropyltrimethoxysilane | 33.5 |
| 3-(2-aminoethyl)-aminopropyltrimethoxysilane | 33.5 |
| poly(styrene) | 34 |
| p-tolyltrimethoxysilane | 34 |
| cianoethyltrimethoxysilane | 34 |
| aminopropyltriethoxysilane | 35 |
| polymethylmethacrylate | 39 |
| polyvinylchloride | 39 |
| phenyltrimethoxysilane | 40.0 |
| chloropropyltrimethoxysilane | 40.5 |
| mercaptopropyltrimethoxysilane | 41 |
| glycidoxypropyltrimethoxysilane | 42.5 |
| poly(ethyleneterephthalate) | 43 |
| poly(ethylene oxide) | 43-45 |
| copper (dry) | 44 |
| aluminum (dry) | 45 |
| iron (dry) | 46 |
| nylon 6/6 | 45-6 |
| glass, soda-lime (dry) | 47 |
| silica, fused | 78 |
| titanium dioxide (anatase) | 91 |
| ferric oxide | 107 |
| tin oxide | 111 |

Note: Critical surface tensions for silanes refer to smooth treated surfaces.

How does a Silane Modify a Surface?

Most of the widely used organosilanes have one organic substituent and three hydrolyzable substituents. In the vast majority of surface treatment applications, the alkoxy groups of the trialkoxysilanes are hydrolyzed to form silanol-containing species. Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile groups 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. Although described sequentially, these reactions can occur simultaneously after the initial hydrolysis step. 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 in condensed or free form. The R group remains available for covalent reaction or physical interaction with other phases.

Silanes can modify surfaces under anhydrous conditions consistent with monolayer and vapor phase deposition requirements. Extended reaction times (4-12 hours) at elevated temperatures (50°-120°C) are typical. Of the alkoxy silanes, only methoxysilanes are effective without catalysis. The most effective silanes for vapor phase deposition are cyclic azasilanes.

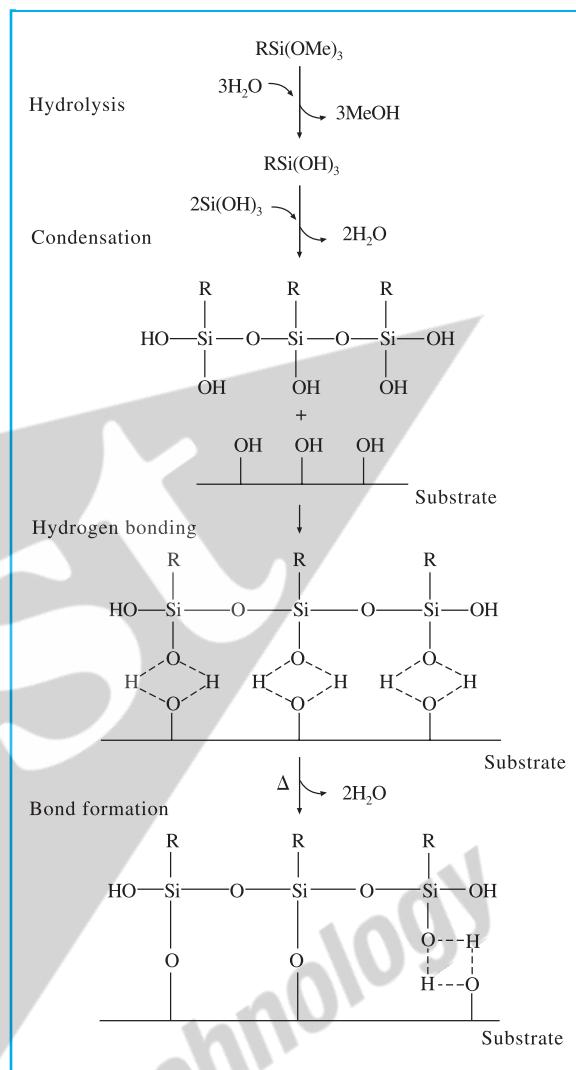
Hydrolysis Considerations

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. The degree of polymerization of the silanes is determined by the amount of water available and the organic substituent. If the silane is added to water and has low solubility, a high degree of polymerization is favored. Multiple organic substitution, particularly if phenyl or tertiary butyl groups are involved, favors formation of stable monomeric silanols.

The thickness of a polysiloxane layer is also determined by the concentration of the siloxane solution. Although a monolayer is generally desired, multilayer adsorption results from solutions customarily used. It has been calculated that deposition from a 0.25% silane solution onto glass could result in three to eight molecular layers. These multilayers could be either interconnected through a loose network structure, or intermixed, or both, and are, in fact, formed by most deposition techniques. The orientation of functional groups is generally horizontal, but not necessarily planar, on the surface of the substrate.

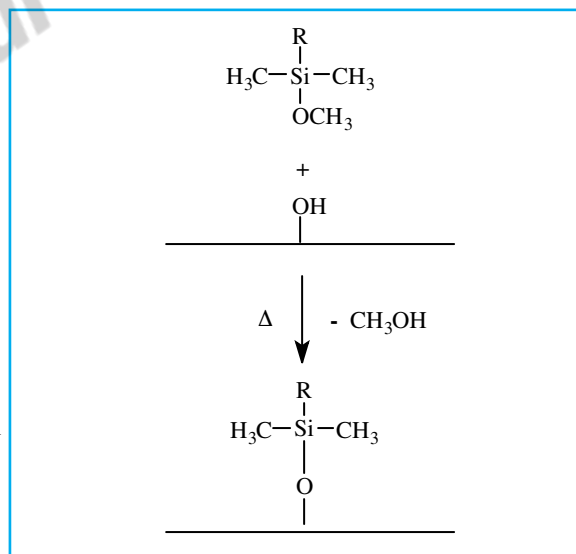
The formation of covalent bonds to the surface proceeds with a certain amount of reversibility. As water is removed, generally by heating to 120°C for 30 to 90 minutes or evacuation for 2 to 6 hours, bonds may form, break, and reform to relieve internal stress.

Hydrolytic Deposition of Silanes



B. Arkles, CHEMTECH, 7, 766, 1977

Anhydrous Deposition of Silanes



Selecting A Silane for Surface Modification - Inorganic Substrate Perspective

Factors influencing silane surface modification selection include:

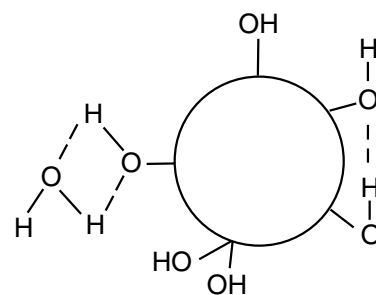
- Concentration of surface hydroxyl groups*
- Type of surface hydroxyl groups*
- Hydrolytic Stability of the bond formed*
- Physical dimensions of the substrate or substrate features*

Surface modification is maximized when silanes react with the substrate surface and present the maximum number of accessible sites with appropriate surface energies. An additional consideration is the physical and chemical properties of the interphase region. The interphase can promote or detract from total system properties depending on its physical properties such as modulus or chemical properties such as water/hydroxyl content.

Hydroxyl-containing substrates vary widely in concentration and type of hydroxyl groups present. Freshly fused substrates stored under neutral conditions have a minimum number of hydroxyls. Hydrolytically derived oxides aged in moist air have significant amounts of physically adsorbed water which can interfere with coupling. Hydrogen bonded vicinal silanols react more readily with silane coupling agents, while isolated or free hydroxyls react reluctantly.

Silanes with three alkoxy groups are the usual starting point for substrate modification. These materials tend to deposit as polymeric films, effecting total coverage and maximizing the introduction of organic functionality. They are the primary materials utilized in composites, adhesives, sealants, and coatings. Limitations intrinsic in the utilization of a polylayer deposition are significant for nano-particles or nano-composites where the interphase dimensions generated by polylayer deposition may approach those of the substrate. Residual (non-condensed) hydroxyl groups from alkoxy-silanes can also interfere in activity. Monoalkoxy-silanes provide a frequently used alternative for nano-featured substrates since deposition is limited to a monolayer.

If the hydrolytic stability of the oxane bond between the silane and the substrate is poor or the application is in an aggressive aqueous environment, dipodal silanes often exhibit substantial performance improvements. These materials form tighter networks and may offer up to 10⁵x greater hydrolysis resistance making them particularly appropriate for primer applications.



Water droplets on a (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane-treated silicon wafer exhibit high contact angles, indicative of the low surface energy. Surfaces are both hydrophobic and resist wetting by hydrocarbon oils. (water droplets contain dye for photographic purposes).

Silane Effectiveness on Inorganics

| | SUBSTRATES |
|-----------|---|
| EXCELLENT | Silica |
| | Quartz |
| | Glass |
| | Aluminum (AlO(OH)) |
| | Alumino-silicates (e.g. clays) |
| | Silicon |
| | Copper |
| | Tin (SnO) |
| | Talc |
| | Inorganic Oxides (e.g. Fe ₂ O ₃ , TiO ₂ , Cr ₂ O ₃) |
| GOOD | Steel, Iron |
| | Asbestos |
| | Nickel |
| | Zinc |
| | Lead |
| SLIGHT | Marble, Chalk (CaCO ₃) |
| | Gypsum (CaSO ₄) |
| | Barytes (BaSO ₄) |
| | Graphite |
| POOR | Carbon Black |

Estimates for Silane Loading on Siliceous Fillers

| Average Particle Size | Amount of Silane (minimum of monolayer coverage) |
|-----------------------|--|
| <1 micron | 1.5% |
| 1-10 microns | 1.0% |
| 10-20 microns | 0.75% |
| >100 microns | 0.1% or less |

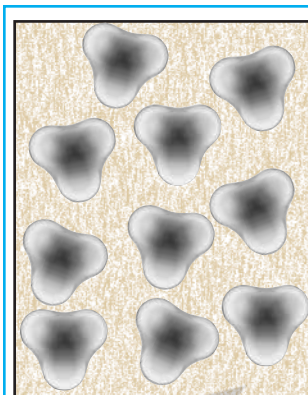
Hydrophobic Silane Surface Treatments

Factors which contribute to the ability of an organosilane to generate a hydrophobic surface are its organic substitution, the extent of surface coverage, residual unreacted groups (both from the silane and the surface) and the distribution of the silane on the surface.

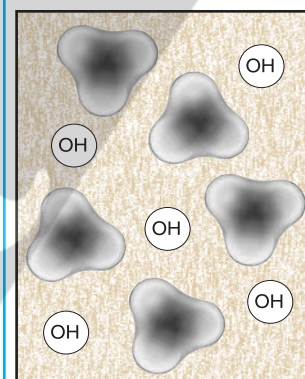
Aliphatic hydrocarbon substituents or fluorinated hydrocarbon substituents are the hydrophobic entities which enable silanes to induce surface hydrophobicity. Beyond the simple attribute that in order to generate a hydrophobic surface the organic substitution of the silane must be non-polar, more subtle distinctions can be made. The hydrophobic effect of the organic substitution can be related to the free energy of transfer of hydrocarbon molecules from an aqueous phase to a homogeneous hydrocarbon phase. For non-polar entities, van der Waals interactions are predominant factors in interactions with water and such interactions compete with hydrogen bonding in ordering of water molecules. Van der Waals interactions for solid surfaces are primarily related to the instantaneous polarizability of the solid which is proportional to the dielectric constant or permittivity at the primary UV absorption frequency and the refractive index of the solid. Entities which present sterically closed structures that minimize van der Waals contact are more hydrophobic than open structures that allow van der Waals contact. Thus, in comparison to polyethylene, polypropylene and polytetrafluoroethylene are more hydrophobic. Similarly methyl-substituted alkylsilanes and fluorinated alkylsilanes provide better hydrophobic surface treatments than linear alkyl silanes.

Surfaces to be rendered hydrophobic usually are polar with a distribution of hydrogen bonding sites. A successful hydrophobic coating must eliminate or mitigate hydrogen bonding and shield polar surfaces from interaction with water by creating a non-polar interphase. Hydroxyl groups are the most common sites for hydrogen bonding. The hydrogens of hydroxyl groups can be eliminated by oxane bond formation with an organosilane. The effectiveness of a silane in reacting with hydroxyls impacts hydrophobic behavior not only by eliminating the hydroxyls as water adsorbing sites, but also by providing anchor points for the non-polar organic substitution of the silane which shields the polar substrates from interaction with water.

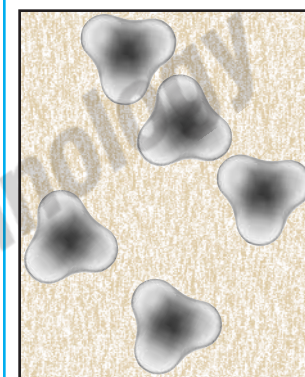
Strategies for silane surface treatment depend on the population of hydroxyl groups and their accessibility for bonding. A simple conceptual case is the reaction of organosilanes to form a monolayer. If all hydroxyl groups are capped by the silanes and the surface is effectively shielded, a hydrophobic surface is achieved. Practically, not all of the hydroxyl groups may react leaving residual sites for hydrogen bonding. Further, there may not be enough anchor points on the surface to allow the organic substituents to effectively shield the substrate. Thus the substrate reactive groups of the silane, the conditions of deposition, the ability of the silane to form monomeric or polymeric layers and the nature of the organic substitution all play a role in rendering a surface hydrophobic. The minimum requirements of hydrophobicity and economic restrictions for different applications further complicate selection.



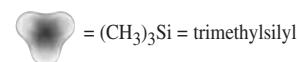
complete coverage



incomplete hydroxyl reaction



few bonding opportunities



Hypothetical Trimethylsilylated Surfaces

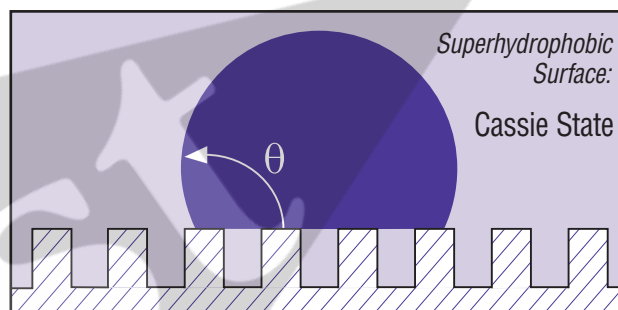
Pyrogenic silica has 4.4-4.6 OH/nm². Typically less than 50% are reacted. Other substrates have fewer opportunities for reaction.

Hydrophobicity is frequently associated with oleophilicity, the affinity of a substance for oils, since non-polar organic substitution is often hydrocarbon in nature and shares structural similarities with many oils. The hydrophobic and oleophilic effect can be differentiated and controlled. At critical surface tensions of 20-30, surfaces are wetted by hydrocarbon oils and are water repellent. At critical surface tensions below 20, hydrocarbon oils no longer spread and the surfaces are both hydrophobic and oleophobic. The most oleophobic silane surface treatments have fluorinated long-chain alkyl silanes and methylated medium chain alkyl silanes.

Superhydrophobic surfaces are those surfaces that present apparent contact angles that exceed the theoretical limit for smooth surfaces, i.e. $>120^\circ$. The most common examples of super-hydrophobicity are associated with surfaces that are rough on a sub-micron scale and contact angle measurements are composites of solid surface asperities and air denoted the *Cassie state*. Perfectly hydrophobic surfaces (contact angles of 180°) have been prepared by hydrolytic deposition of methylchlorosilanes as microfibrillar structures.

Hydrophobicity vs Water Permeability

Although silane and silicone derived coatings are in general the most hydrophobic, they maintain a high degree of permeability to water vapor. This allows coatings to breathe and reduce deterioration at the coating interface associated with entrapped water. Since ions are not transported through non-polar silane and silicone coatings, they offer protection to composite structures ranging from pigmented coatings to rebar reinforced concrete.



Automotive side windows are treated with fluoroalkylsilanes to provide self-cleaning properties. Water beads remove soil as they are blown over the glass substrate during acceleration.

Hydrophilic Silane Surface Treatments

The vast majority of surfaces are hydrophilic and water is omnipresent in the environment, yet the precise nature of interaction of water with specific surfaces is largely unknown. Water adsorption may be uniform or in isolated patches. It may be driven by a number of different physical and chemical processes. The adsorption of water by a surface may be assisted or retarded by other adsorbents present in the environment. The purpose of applying a hydrophilic surface treatment is to control the nature and extent of interaction of water with a surface.

The controlled interaction of water with substrates can offer various degrees of hydrophilicity ranging from physisorption to chemisorption and centers for ion-interaction. The utility of hydrophilic surfaces varies widely. Anti-fog coatings exploit high surface energies to flatten water droplets rather than allowing them to form light-scattering droplets. In biological systems hydrophilic surfaces can reduce nonspecific bonding of proteins. Hydrophilic coatings with hydrogen bonding sites allow formation of tightly adherent layers of water with high lubricity in biological systems and the ability to resist oil adsorption in anti-graffiti coatings. They can also be used to disperse particles in aqueous coatings and oil-in-water emulsions. Hydrophilic coatings with ionic sites form antistatic coatings, dye receptive surfaces and can generate conductive or electrophoretic pathways. Thick films can behave as polymeric electrolytes in battery and ion conduction applications.

In general, surfaces become more hydrophilic in the series: non-polar < polar, no hydrogen-bonding < polar, hydrogen-bonding < hydroxylic, < ionic. The number of sites and the structure and density of the interphase area also have significant influence on hydrophilicity.

Much of the discussion of hydrophobicity centers around high contact angles and their measurement. As a corollary, low or 0° contact angles of water are associated with hydrophilicity, but practically the collection of consistent data is more difficult. Discriminating between surfaces with a 0° contact angle is impossible. The use of heat of immersion is a method that generates more consistent data for solid surfaces, provided they do not react with, dissolve or absorb the tested liquid. Another important consideration is whether water adsorbed is “free” or “bound.” Free water is water that is readily desorbed under conditions of less than 100% relative humidity. If water remains bound to a substrate under conditions of less than 100% relative humidity, the surface is considered hygroscopic. Another description of hygroscopic water is a boundary layer of water adsorbed on a surface less than 200nm thick that cannot be removed without heating. A measure of the relative hygroscopic nature of surfaces is given by the water activity, the ratio of the fugacity, or escaping tendency, of water from a surface compared to the fugacity of pure water.

The hydrophilicity of a surface as measured or determined by contact angle is subject to interference by loosely bound oils and other contaminants. Heats of immersion and water activity measurements are less subject to this interference. Measurements of silane-modified surfaces demonstrate true modification of the intrinsic surface properties of substrates. If the immobilized hydrophilic layer is in fact a thin hydrogel film, then swelling ratios at equilibrium water absorption can provide useful comparative data.

Anti-fog coatings applied to one side of a visor can be prepared from combinations of polyalkylene oxide functional silanes and film-forming hydrophilic silanes.



Heats of Immersion in Water, mJ/m²

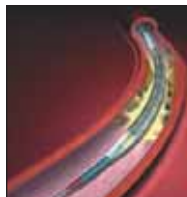
| | |
|---------------------------------|---------|
| titanium dioxide | 225-250 |
| talc | 220-260 |
| aminopropyltriethoxysilane* | 230-270 |
| silicon dioxide | 210-225 |
| glass | 200-205 |
| vinyltris(methoxyethoxy)silane* | 110-190 |
| mercaptopropyltrimethoxysilane* | 80-170 |
| graphite | 32-35 |
| polytetrafluoroethylene | 24-25 |

*Data for silane treated surfaces in this table is primarily from B. Marciniec et al, Colloid & Polymer Science, 261, 1435, 1983 recalculated for surface area.

Hydrophilic Silane Surface Treatments (continued)

Controlling hydrophilic interaction with silane surface treatments is accomplished by the selection of a silane with the appropriate hydrophilic substitution. The classes of substitution are:

- Polar, Non-Hydrogen Bonding
- Polar, Hydrogen-Bonding
- Hydroxylic
- Ionic-Charged



Aortic stents are coated to promote hydrophilicity, coupling to polymers and drug delivery systems.

The selection of the class of hydrophilic substitution is dependent on the application. If it is sufficient for water to spread evenly over a surface to form a thin film that washes away and dries off quickly without leaving 'drying spots', then a polar aprotic silane is preferred. If a coating is desired that reduces non-specific binding of proteins or other biofoulants, then a polar hydrogen-bonding material such as a polyether functional silane is preferred. A very different application for a polar non-hydroxylic materials is thin film proton conduction electrolytes. Lubricious coatings are usually hydroxylic since they require a restrained adsorbed phase of water. Antistatic coatings are usually charged or charge-inducible as are ion-conductive coatings used in the construction of thin-film batteries. A combination of hydrophilicity and hydrophobicity may be a requirement in coatings which are used as primers or in selective adsorption applications such as chromatography. Formulation limitations may require that hydrophilicity is latent and becomes unmasked after application.

Factors affecting the intrinsic hydrolytic stability of silane treated surfaces are magnified when the water is drawn directly into the interface. Even pure silicon dioxide is ultimately soluble in water (at a level of 2-6ppm), but the kinetics, low concentration for saturation and phase separation, make this a negligible consideration in most applications. The equilibrium constant for the rupture of a Si-O-Si bond by water to two Si-OH bonds is estimated at 10^{-3} . Since at minimum 3 Si-O-Si bonds must be simultaneously broken under equilibrium conditions to dissociate an organosilane from a surface, in hydrophobic environments the long-term stability is a minor consideration. Depending on the conditions of exposure to water of a hydrophilic coating, the long-term stability can be an important consideration. Selection of a dipodal, polyodal or other network forming silane as the basis for inducing hydrophilicity or as a component in the hydrophilic surface treatment is often obligatory.

Range of Water Interaction with Surfaces

| interaction | description | surface example | measurement - parameter |
|-------------|-------------------|--------------------------|---|
| low | superhydrophobic | fluorocarbon | contact angle |
| | oleophobic | | |
| | lipophobic | | |
| | oleophilic | | |
| | lipophilic | | |
| moderate | hydrophobic | hydrocarbon | water-sliding angle critical surface tension |
| | polar hydrophilic | polymer oxide surface | heat of immersion |
| | hygroscopic | polyhydroxylic | water activity |
| | strong | hydrogel film | equilibrium water absorption swell |

Reacting with the Substrate

Leaving Groups

The reaction of an organofunctional silane with a surface bearing hydroxyl group results in a substitution reaction at silicon and the formation of the silylated surface where the silicon is covalently attached to the surface via an oxygen linkage. This connection may be formed directly or in the presence of water through a reactive silanol intermediate. In general the reactivity of hydroxylated surfaces with organofunctional silanes decreases in the order: $\text{Si-NR}_2 > \text{Si-Cl} > \text{Si-NH-Si} > \text{Si-O}_2\text{CCH}_3 > \text{Si-OCH}_3 > \text{Si-OCH}_2\text{CH}_3$. An analysis of the relevant bond energies indicates that the formation of the Si-O-surface bond is the driving force for the reaction under dry and aprotic conditions. Secondary factors contributing to the reactivity of organofunctional silanes with a surface are the volatility of the byproducts, the ability of the byproduct to hydrogen bond with the hydroxyls on the surface, the ability of the byproduct to catalyze further reactions, e.g. HCl or acetic acid, and the steric bulk of the groups on the silicon atom.

Although they are not the most reactive organosilanes, the methoxy and ethoxysilanes are the most widely used organofunctional silanes for surface modification. The reasons for this include the fact that they are easily handled and the alcohol byproducts are non-corrosive and volatile. The methoxysilanes are capable of reacting with substrates under dry, aprotic conditions, while the less reactive ethoxysilanes require catalysis for suitable reactivity. The low toxicity of ethanol as a byproduct of the reaction favors the ethoxysilanes in many commercial applications. The vast majority of organofunctional silane surface treatments are performed under conditions in which water is a part of the reaction medium, either directly added or contributed by adsorbed water on the substrate or atmospheric moisture.

Bond Dissociation Energies

| Bond | Dissociation Energy (kcal/mole) |
|---|---------------------------------|
| $\text{Me}_3\text{Si-NMe}_2$ | 98 |
| $\text{Me}_3\text{Si-N}(\text{SiMe}_3)_2$ | 109 |
| $\text{Me}_3\text{Si-Cl}$ | 117 |
| $\text{Me}_3\text{Si-OMe}$ | 123 |
| $\text{Me}_3\text{Si-OEt}$ | 122 |
| $\text{Me}_3\text{Si-OSiMe}_3$ | 136 |

Common Leaving Groups

| Type | Advantage | Disadvantage |
|----------------------------|--|----------------------|
| dimethylamine | reactive, volatile byproduct | toxic |
| hydrogen chloride | reactive, volatile byproduct | corrosive |
| silazane (NH_3) | volatile | limited availability |
| methoxy | moderate reactivity, neutral byproduct | moderate toxicity |
| ethoxy | low toxicity | lower reactivity |

Special Topics

Dipodal Silanes

Functional dipodal silanes and combinations of non-functional dipodal silanes with functional silanes have significant impact on substrate bonding, hydrolytic stability and mechanical strength of many composites systems. They possess enabling activity in many coatings, particularly primer systems and aqueous immersion applications. The effect is thought to be a result of both the increased crosslink density of the interphase and a consequence of the fact that the resistance to hydrolysis of dipodal materials (with the ability to form six bonds to a substrate) is estimated at close to 100,000 times greater than conventional coupling agents (with the ability to form only three bonds to a substrate).

Both because dipodal silanes may not have functional groups identical to conventional coupling agents or because of economic considerations, conventional coupling agents are frequently used in combination with a non-functional dipodal silanes. In a typical application a dipodal material such as bis(triethoxysilyl)ethane (SIB1817.0) is combined at a 1:5 to 1:10 ratio with a traditional coupling agent. It is then processed in the same way as the traditional silane coupling agent.

Effect of dipodal -SiCH₂CH₂Si- on the bond strength of a crosslinkable ethylene-vinyl acetate primer formulation

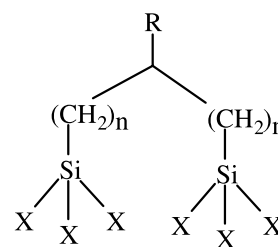
| Primer on metal 10% in <i>i</i> -PrOH | Wet adhesion to metals (N/cm) | |
|--|-------------------------------|----------------------------|
| | Titanium | Cold-rolled steel |
| No silane | Nil | Nil |
| Methacryloxypropylsilane | 0.25 | 7.0 |
| Methacryloxypropylsilane + 10% dipodal | 10.75 | 28.0 (cohesive failure) |

90° peel strength after 2 h in 80°C water.

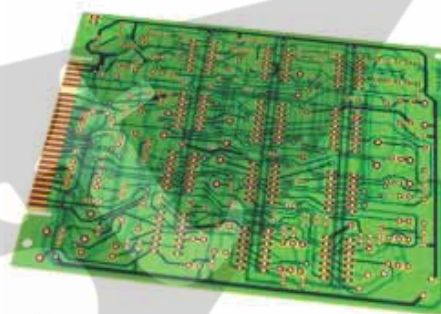
P. Pape et al, in *Silanes and Other Coupling Agents*, ed. K. Mittal, 1992, VSP, p105



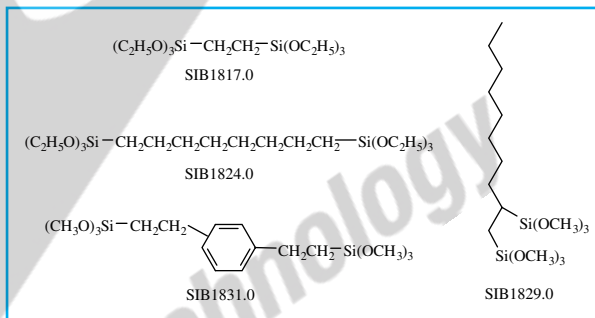
Hydrophobic coatings applied to antennas inhibit the formation of adsorbed water layers which become dielectric layers that absorb signals and cause high losses. If the water is in beads, the energy will be slightly diffracted because the water droplets have dimensions much less than a wavelength at these frequencies.



Multilayer printed circuit boards use dipodal silanes to maintain the integrity of the bond between metal and resins by reducing interfacial water adsorption.



Hydrophobic Dipodal Silanes



Hydrophilic Dipodal Silanes

