

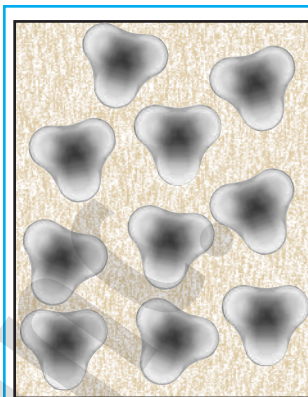
Hydrophobic Silane Surface Treatments

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.

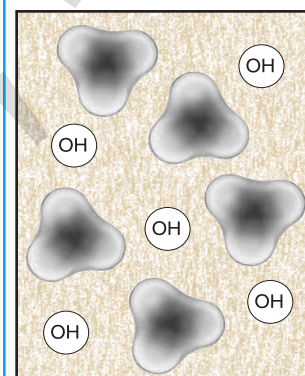
Aliphatic hydrocarbon substituents or fluorinated hydrocarbon substituents are the hydrophobic entities which enable silanes to induce surface hydrophobicity. Beyond the simple attribute that in order to generate a hydrophobic surface the organic substitution of the silane must be non-polar, more subtle 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.

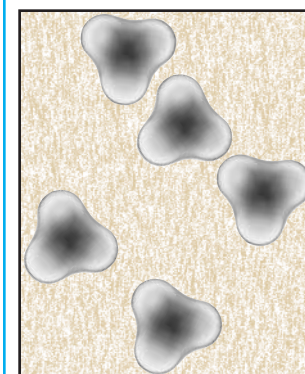
Strategies for silane surface treatment depend on the population of hydroxyl groups and their accessibility for bonding. A simple conceptual case is the reaction of organosilanes to form a monolayer. If all hydroxyl groups are capped by the silanes and the surface is effectively shielded, a hydrophobic 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.



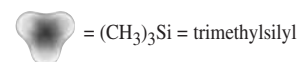
complete coverage



incomplete hydroxyl reaction



few bonding opportunities



Hypothetical Trimethylsilylated Surfaces

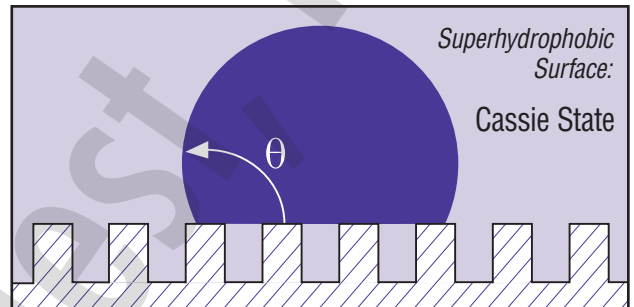
Pyrogenic silica has 4.4-4.6 OH/nm². Typically less than 50% are reacted. Other substrates have fewer opportunities for reaction.

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.



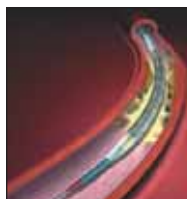
Heats of Immersion in Water, mJ/m²	
titanium dioxide	225-250
talc	220-260
aminopropyltriethoxysilane*	230-270
silicon dioxide	210-225
glass	200-205
vinyltris(methoxyethoxy)silane*	110-190
mercaptopropyltrimethoxysilane*	80-170
graphite	32-35
polytetrafluoroethylene	24-25

*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, polypodal 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		contact angle
	oleophobic	fluorocarbon	
	lipophobic		
	oleophilic		water-sliding angle
	lipophilic	hydrocarbon	critical surface tension
moderate	hydrophobic		
	polar hydrophilic	polymer oxide surface	heat of immersion
	hygroscopic	polyhydroxylic	water activity
strong	hydrogel film		equilibrium water absorption swell