

Applying Silanes

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 mins at 110°C or 24 hours at room temperature (<60% relative humidity).

Fig. 1 Reactor for slurry treatment of powders. Separate filtration and drying steps are required.



Deposition from aqueous solution is employed for most commercial fiberglass systems. The alkoxysilane 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. 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 2-12 hours for the simple alkyl silanes. 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 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.

Fig. 2 Vacuum tumble dryers can be used for slurry treatment of powders.



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 alkoxysilanes to dry-blends of polymer and filler prior to compounding. Generally 0.2 to 1.0 weight percent of silane (of 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 benzyldimethylamine to the silane prior to dispersal.

Anhydrous liquid phase deposition of chlorosilanes, methoxysilanes, aminosilanes and cyclic azasilanes is preferred for small particles and nano-featured substrates. 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 predried 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.

Chlorosilanes can also 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 alkoxysilane 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 alkoxysilanes. The silanols condense on the substrate. Treated substrates are cured for 5-10 mins. at 110°C or allowed to stand 24 hours at room temperature.



Fig. 3 Twin-cone blenders with intensive mixing bars are used for bulk deposition of silanes onto powders.

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Vapor Phase Deposition

Silanes can be applied to substrates under dry aprotic conditions by chemical vapor deposition methods. These methods favor monolayer deposition. Although under proper conditions almost all silanes can be applied to substrates in the vapor phase, those with vapor pressures >5 torr at 100°C have achieved the greatest number of commercial applications. In closed chamber designs, substrates are supported above or adjacent to a silane reservoir and the reservoir is heated to sufficient temperature to achieve 5mm vapor pressure. Alternatively, vacuum can be applied until silane evaporation is observed. In still another variation the silane can be prepared as a solution in toluene, and the toluene brought to reflux allowing sufficient silane to enter the vapor phase through partial pressure contribution. In general, substrate temperature should be maintained above 50° and below 120° to promote reaction. Cyclic azasilanes deposit the quickest—usually less than 5 minutes. Amine functional silanes usually deposit rapidly (within 30 minutes) without a catalyst. The reaction of other silanes requires extended reaction times, usually 4-24 hours. The reaction can be promoted by addition of catalytic amounts of amines.

Spin-On

Spin-On applications can be made under hydrolytic conditions which favor maximum functionalization and polylayer deposition or dry conditions which favor monolayer deposition. For hydrolytic deposition 2-5% solutions are prepared (see deposition from aqueous alcohol). Spin speed is low, typically 500 rpm. Following spin-deposition a hold period of 3-15 minutes is required before rinse solvent. Dry deposition employs solvent solutions such as methoxypropanol or ethyleneglycol monoacetate (EGMA). Aprotic systems utilize toluene or THF. Silane solutions are applied at low speed under a nitrogen purge. If strict monolayer deposition is preferred, the substrate should be heated to 50° . In some protocols, limited polylayer formation is induced by spinning under an atmospheric ambient with 55% relative humidity.

Spray application

Formulations for spray applications vary widely depending on end-use. They involve alcohol solutions and continuously hydrolyzed aqueous solutions employed in architectural and masonry applications. The continuous hydrolysis is effected by feeding mixtures of silane containing an acid catalyst such as acetic acid into a water stream by means of a venturi (aspirator). Stable aqueous solutions (see water-borne silanes), mixtures of silanes with limited stability (4-8 hours) and emulsions are utilized in textile and fiberglass applications. Complex mixtures with polyvinyl acetates or polyesters enter into the latter applications as sizing formulations.

Figure 4.
Apparatus for vapor phase silylation.

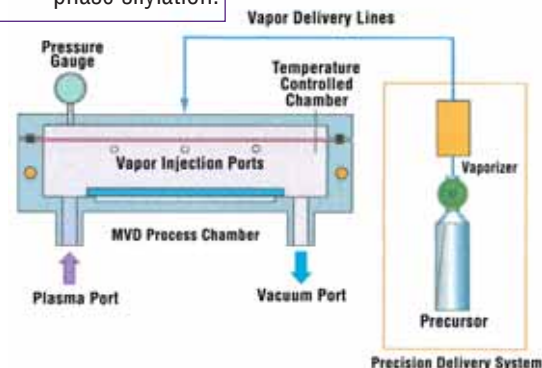


Figure 5.
Spin-coater
for deposition
on wafers.



Figure 6.
Spray
application
of silanes
on large
structures.



Figure 7.
Spray &
contact roller
application of
silanes on
fiberglass.

