

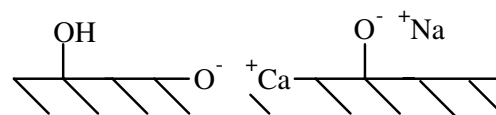
Difficult Substrates

Silane coupling agents are generally recommended for applications in which an inorganic surface has hydroxyl groups and the hydroxyl groups can be converted to stable oxane bonds by reaction with the silane. Substrates such as calcium carbonate, copper and ferrous alloys, and high phosphate and sodium glasses are not recommended substrates for silane coupling agents. In cases where a more appropriate technology is not available a number of strategies have been devised which exploit the organic functionality, film-forming and crosslinking properties of silane coupling agents as the primary mechanism for substrate bonding in place of bonding through the silicon atom. These approaches frequently involve two or more coupling agents.

Calcium carbonate fillers and marble substrates do not form stable bonds with silane coupling agents. Applications of mixed silane systems containing a dipodal silane or tetraethoxysilane in combination with an organofunctional silane frequently increases adhesion. The adhesive mechanism is thought to be due to the low molecular weight and low surface energy of the silanes which allows them initially to spread to thin films and penetrate porous structures followed by the crosslinking which results in the formation of a silica-rich encapsulating network. The silica-rich encapsulating network is then susceptible to coupling chemistry comparable to siliceous substrates. Marble and calciferous substrates can also benefit from the inclusion of anhydride-functional silanes which, under reaction conditions, form dicarboxylates that can form salts with calcium ions.

Metals and many metal oxides can strongly adsorb silanes if a chelating functionality such as diamine or dicarboxylate is present. A second organofunctional silane with reactivity appropriate to the organic component must be present. Precious metals such as gold and rhodium form weak coordination bonds with phosphine and mercaptan functional silanes.

High phosphate and sodium content glasses are frequently the most frustrating substrates. The primary inorganic constituent is silica and would be expected to react readily with silane coupling agents. However alkali metals and phosphates not only do not form hydrolytically stable bonds with silicon, but, even worse, catalyze the rupture and redistribution of silicon-oxygen bonds. The first step in coupling with these substrates is the removal of ions from the surface by extraction with deionized water. Hydrophobic dipodal or multipodal silanes are usually used in combination with organofunctional silanes. In some cases polymeric silanes with multiple sites for interaction with the substrate are used. Some of these, such as the polyethylenimine functional silanes can couple to high sodium glasses in an aqueous environment.



Substrates with low concentrations of non-hydrogen bonded hydroxyl groups, high concentrations of calcium, alkali metals or phosphates pose challenges for silane coupling agents.

Removing Surface Impurities

Eliminating non-bonding metal ions such as sodium, potassium and calcium from the surface of substrates can be critical for stable bonds. Substrate selection can be essential. Colloidal silicas derived from tetraethoxysilane or ammonia sols perform far better than those derived from sodium sols. Bulk glass tends to concentrate impurities on the surface during fabrication. Although sodium concentrations derived from bulk analysis may seem acceptable, the surface concentration is frequently orders of magnitude higher. Surface impurities may be reduced by immersion in 5% hydrochloric acid for 4 hours, followed by a deionized water rinse, and then immersion in deionized water overnight followed by drying.

Oxides with high isoelectric points can adsorb carbon dioxide, forming carbonates. These can usually be removed by a high temperature vacuum bake.

Increasing Hydroxyl Concentration

Hydroxyl functionalization of bulk silica and glass may be increased by immersion in a 1:1 mixture of 50% aqueous sulfuric acid : 30% hydrogen peroxide for 30 minutes followed by rinses in D.I. water and methanol and then air drying. Alternately, if sodium ion contamination is not critical, boiling with 5% aqueous sodium peroxodisulfate followed by acetone rinse is recommended¹.
1. K. Shirai et al, J. Biomed. Mater. Res. 53, 204, 2000.

Catalyzing Reactions in Water-Free Environments

Hydroxyl groups without hydrogen bonding react slowly with methoxy silanes at room temperature. Ethoxy silanes are essentially non-reactive. The methods for enhancing reactivity include transesterification catalysts and agents which increase the acidity of hydroxyl groups on the substrate by hydrogen bonding. Transesterification catalysts include tin compounds such as dibutyltin diacetate and titanates such as titanium isopropoxide. Incorporation of transesterification catalysts at 2-3 weight % of the silane effectively promotes reaction and deposition in many instances. Alternatively, amines can be premixed with solvents at 0.01-0.5 weight % based on substrate prior or concurrent to silane addition. Volatile primary amines such as butylamine can be used, but are not as effective as tertiary amines such as benzyltrimethylamine or diamines such as ethylenediamine. The more effective amines, however, are more difficult to remove after reaction¹.
1. S. Kanan et al, Langmuir, 18, 6623, 2002.

Hydroxylation by Water Plasma & Steam Oxidation

Various metals and metal oxides including silicon and silicon dioxide can achieve high surface concentrations of hydroxyl groups after exposure to H₂O/O₂ in high energy environments including steam at 1050° and water plasma¹.

1. N. Alcanter et al, in "Fundamental & Applied Aspects of Chemically Modified Surfaces" ed. J. Blitz et al, 1999, Roy. Soc. Chem., p212.