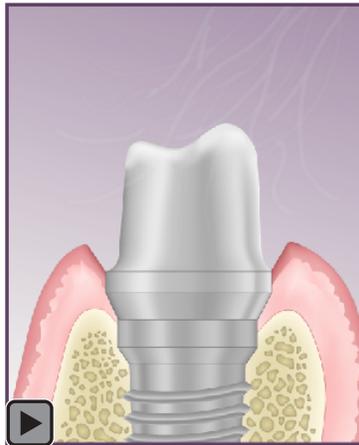


## Silane Based Concepts on Bonding Resin Composite to Metals

Jukka P. Matinlinna, PhD, MSc; Pekka K. Vallittu, PhD, DDS, CDT, Prof



### Abstract

**Introduction:** The longevity of silane promoted adhesion of surface conditioned metallic materials is of concern in dentistry and poses both a functional and esthetic dilemma for the patient and dental professionals. Several methods for surface conditioning exist, but some are employed more frequently in clinical practice.

**Aim of the Review:** This overview aims to characterize and discuss the most commonly used surface conditioning methods based on silanization. The primary chemical features in silane treatment will also be presented.

**Method of Review:** The literature regarding silane utilization was systematically selected and 68 cited references published during 1967-2005 were reviewed. Technical descriptions of different silica-coating (silicatization) methods are presented and some comparative clinical and *in vitro* experiences are reported. Some other surface condition methods applied in dental laboratories were also selected for presentation.

**Conclusion:** It is concluded in this overview tribochemical silica-coating followed by a mandatory silane coupling agent application is a clinically proved, relevant adhesion promotion method to enhance the bonding of resin composites to metallic dental materials.

**Keywords:** Silica-coating, silane coupling agent, adhesion, noble alloys, base metal alloys, silanization, dental materials

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## Introduction

The problem of a clinically sustainable connection between metal and veneering resin composite which would be stable in the oral environment has been a constant topic in crown and bridge prosthetics for the last two decades. The purpose of this overview article is to provide an insight on the clinical surface conditioning methods for metals combined with silanization procedures. The particular emphasis of this presentation is on the chemical principles of silanization and a concise description of experimental and clinical data.

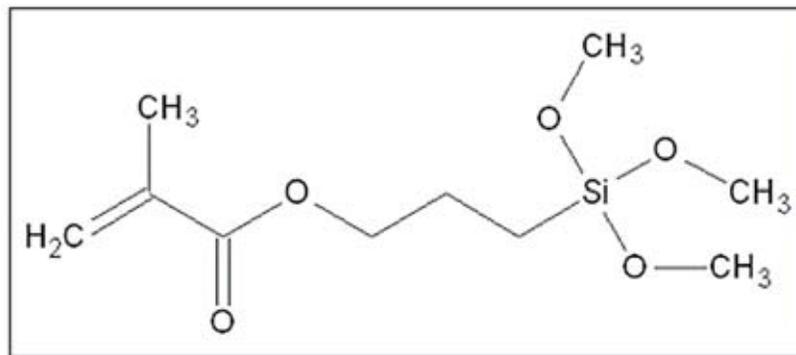


Some of these conditioning methods are currently less trendy, but it might be useful to recognize them. It is well understood the clinical success of modern adhesive restorations depends on the bonding of material phases of the restoration to each other and on the bonding of the restoration to tooth structure.<sup>1</sup> Dental materials and their contact surfaces are subject to stresses in the hostile conditions of the mouth. In order to improve the bonding of material phases in restorative procedures specific conditioning methods have been developed.<sup>2</sup>

In general, conditioning is defined as the treatment of a surface to increase its critical surface energy.<sup>3</sup> The surface energy of a coating, namely a primer or a silane, must overcome the surface energy of the substrate surface.<sup>4</sup> There are two approaches typically used in dentistry: physico-chemical and pure chemical conditioning.<sup>5</sup> Use of a particular surface conditioning technique may also introduce micromechanical features into the substrate, namely acid etching of the dental enamel or etchable ceramics.<sup>6</sup>

The most commonly used surface modifiers in numerous applications in dental technology are silane coupling agents (silanes). They have the characteristic property to bond both inorganic and organic dissimilar materials together.<sup>7</sup> In general, silanes form a large chemical group of hybrid inorganic-organic compounds containing direct  $\equiv\text{Si}-\text{C}\equiv$  bonds.<sup>8</sup> In the dental sciences, silanes are used in resin-based composites for filler surface modification, as a coupling agent for composites to composite surfaces, and to condition ceramic and silica-coated (silicized) partially fixed prosthetic metals.<sup>7</sup> The most familiar silane, 3-methacryloyloxypropyltrimethoxysilane (MPS, or 3-MPS; Figure 1) has been evaluated with filler particles of resin composites<sup>9</sup> and in lamination of glass fibers.<sup>10</sup>

The best fit of MPS in chemical terms to resin composite systems containing  $>\text{C}=\text{C}<$  double bonds in the resin matrix due to its functional polymerizable methacrylate end-group.<sup>7</sup> The first reported findings of silane treatment have been encouraging, but the sensitivity of silanes to the working conditions and in particular to humidity



**Figure 1.** The 3-methacryloyloxypropyltrimethoxysilane silane coupling agent.

became apparent.<sup>11</sup> It has also been shown MPS has adhesion enhancing properties for attaching porcelain teeth to acrylic denture resin.<sup>12</sup>

## Surface Conditioning

### Definition of Conditioning

Conditioning can be defined as treatment of a surface that increases its critical surface energy for adhesion. The concept of critical surface energy is highly significant since the surface tension of a liquid is less than the critical surface energy of a particular surface then the contact angle will be 0 degrees and spontaneous spreading of the liquid will occur.<sup>13</sup> It must be noted critical surface energy is dependent on the surface roughness and morphology, as well as the chemical composition of the substrate.<sup>4</sup> Therefore, a high critical surface energy should be desirable because it will tend to result in more wetting.<sup>13</sup> In many cases the surface may contain low-energy contaminants such as grease, oil, and proteins which need to be removed prior to any bonding procedure. For a bonding agent to be clinically successful some requirements need to be met such as (1) adequate wetting of the substrate with the bonding agent (silane coupling agent) and (2) the presence of adequate micromechanical retention and resistance to fatigue, erosion, and stress relief.<sup>1,5</sup>

### The Role of Silane Coupling Agents and Conditioning

Surface conditioning methods in conjunction with the silanization of filler particles, glass fibers, and ceramic surfaces prior to either luting or the repair of fractured ceramic surfaces such as porcelain-fused-to-metal<sup>14</sup> has been intensively evaluated. This emphasizes the importance of the role of a silane coupling agent in the promotion of adhesion.<sup>5,15</sup>

In general, silane coupling agents used for surface pretreatment to promote adhesion are usually organofunctional trialkoxy silane esters of the general formula R-Y-SiX<sub>3</sub>, where R is a non-hydrolyzable organic group, Y is a linker, typically a propylene link -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and Xs are hydrolyzable groups.<sup>16</sup>

Silanes are chemically bifunctional. The non-hydrolyzable organofunctional group with a

carbon-carbon double bond can polymerize with monomers and repair resin composites which contain similar double bonds.<sup>17,18</sup> The other end of a reactive silane molecule, consisting of the hydrolyzable alkoxy groups, such as methoxy -O-CH<sub>3</sub>, react with an inorganic hydroxyl-rich (-OH) surface.<sup>7</sup> Such surfaces are silica-coated (SiO<sub>2</sub>) metal surfaces. Alkoxy groups are intermediates in the formation of silanol groups, ≡Si-OH.<sup>19</sup>

Silanes are typically used with success as filler surface treatment agents in resin composite technology or as other surface modification agents depending on their functionality and on the technical application.<sup>20</sup>

### Silanization in Practice

It is generally accepted hydrophobic silanes must first be hydrolyzed (activated) in a water-alcohol solution due to their solubility in organic solvents, and then deposited onto the inorganic substrate.<sup>10</sup> Activated silane coupling agents with three alkoxy groups tend to deposit as polymeric siloxane films, maximizing the appearance of organic functionality.<sup>21,22</sup> In an aqueous solution the alkoxy groups react with water to form reactive labile acidic silanol groups, ≡Si-OH.<sup>16,17</sup> Hydrolysis (activation) has been suggested as a crucial step in the adsorption onto an inorganic substrate covered with OH-groups. Activated silanes with silanols are adsorbed, deposited, polymerized, and finally covalently bonded to the substrate surface. This procedure is called silanization or silanation.<sup>23</sup> Silane solution has the highest stability usually at the pH value range of 4-5. However, the pH value is dependent on the silane and its chemical type.<sup>8</sup> The rate of condensation between silanol groups of monomeric silane molecules to larger oligomers is then at the minimum. The reaction can be presented<sup>22</sup> in a simplified way as follows:



where: R is a non-hydrolyzable organic group and Y is a linker (see text above)

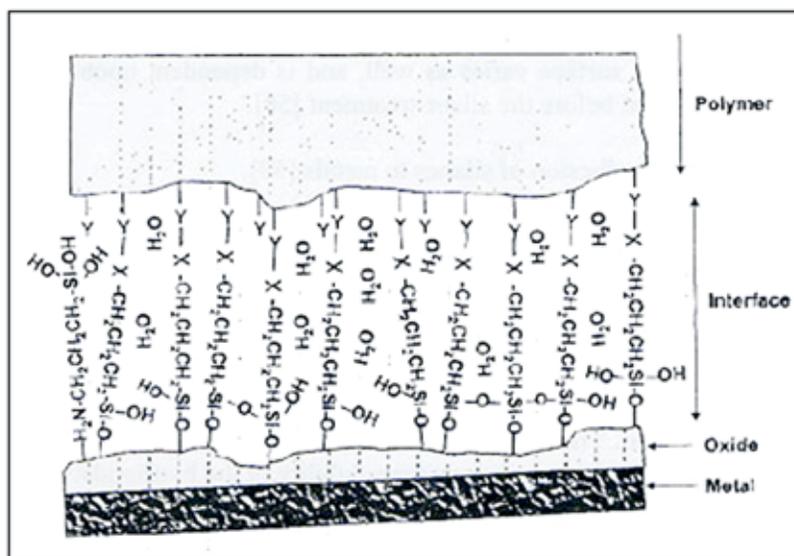
However, complete hydrolysis is not necessary and siloxane films of adequate bonding quality can still be formed since the remaining non-

hydrolyzed alkoxy groups are assumed to become hydrolyzed in air and, thus, activated.<sup>16,24</sup>

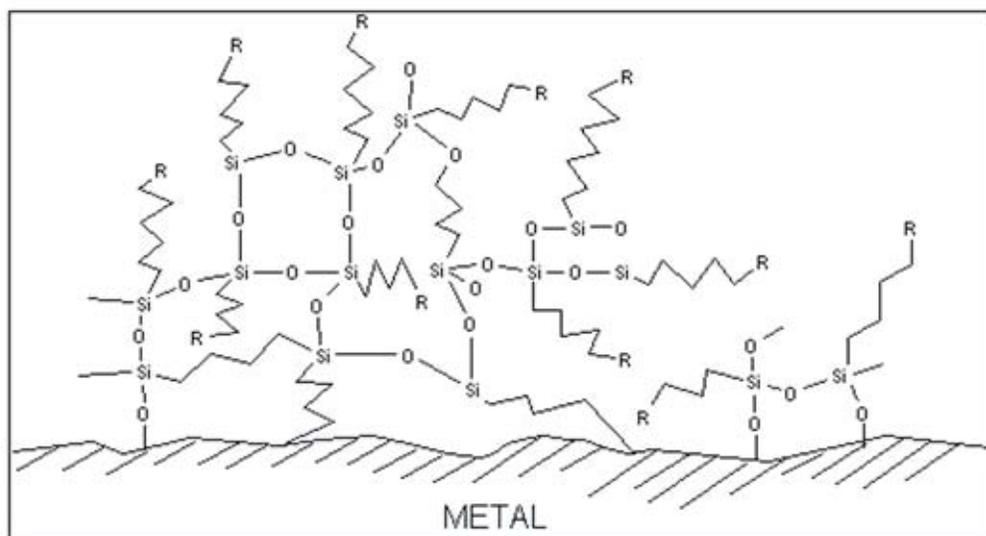
As an actual result of silanization, silanes form a hydrophobic and branched three-dimensional siloxane film between the materials (Figure 2).

It may also contain free hydrogen bonded silane oligomers (Figure 3).

A typical thickness is approximately 10-50 nm, but the thickness is mainly dependent on the silane solution concentration and on the curing conditions.<sup>22,25</sup> It has been concluded thick siloxane films may lead to a cohesive type of failure while insufficient film thickness may lead to poor contact between the silanized inorganic substrate and the polymeric organic matrix.<sup>26</sup> It should be strongly emphasized without any silane



**Figure 2.** A schematic illustration of a siloxane film on a silica-coated metal substrate. The siloxane film is presented as a monolayer. (Courtesy of Professor Wim van Ooij, University of Cincinnati, OH, USA, 2002)



**Figure 3.** A three-dimensional branched siloxane film: the situation in reality. (Courtesy of Dr. Mervi Puska, University of Turku, Finland, 2004)

application the shear bond strength values in all examples presented in this overview would be only 65% or less compared to those obtained with silanization.<sup>27-29</sup>

### Commercially Available Dental Silanes

The silane coupling agent most commonly employed in dental applications is MPS. It is diluted in acidified ethanol-water solution, typically as a 1-5 vol.-% solution, and adjusted at a pH of 4-5 since the silane activation requires that pH.<sup>21</sup> MPS is used to optimize and promote the adhesion between metal-to-composite, ceramic-to-composite, and composite-to-composite substances.<sup>7,30</sup> Over time, silanes can precipitate out of solution forming a siloxane-silicone polymer without coupling properties.<sup>31</sup> It is noted the application of a silane coupling agent may be followed by the use of certain chemical primers in some clinical protocols.<sup>22</sup>

### Metal Surface Conditioning Methods in Dentistry

#### Acid Etching and Electrolytical Coating

One problem facing prosthodontics has been to improve the quality of the bond between metal and veneer materials. A solution was introduced in which the base metal alloy of fixed partial dentures could be electrolytically etched to enhance the adhesion of resin composite luting cements by creating irregularities on the metal surface.<sup>33,34</sup> The acid, electrolyte, current density, and etching time were chosen according to the alloy type in question. Typical alloys were nickel-chromium (Ni-Cr), nickel-chromium-beryllium (Ni-Cr-Be), and cobalt-chromium-molybdenum (Co-Cr-Mo).<sup>1</sup> A properly etched metal surface can be maximally wetted and covered with liquid resin. A high bond strength can be obtained, but the method is vulnerable to contamination and applicable only to a limited number of alloys. Furthermore, the etched surface is difficult to assess with the naked eye.<sup>35</sup>



Acid Etching

Electrolytical tin-plating can also be used for the modification of metal surfaces before

veneering a metal crown.<sup>36</sup> Tin-plating following sandblasting of the alloy surface forms small tin crystals. Tin-plating enhances the micro-mechanical bond achieved with sandblasting and provides micromechanical retention for the resin composite luting cement. The tin-coating is then oxidized and covered with an opaquer resin layer. Generally noble and base alloys can be tin-coated, but the disadvantages are similar to the electrolytically etched surfaces mentioned above.<sup>33,34</sup>

A modified technique, the OVST<sup>TM</sup> system (De Trey Dentsply, Konstanz, Germany), was presented in 1984 for metal fixed partial dentures and crowns.<sup>36</sup> OVST<sup>TM</sup> is based on macromechanical retention achieved by electrolytical tin coating in a tin-salt bath. The tin layer is then oxidized with hydrogen peroxide. Chemical bonding is created with a silane application to a resin composite, such as veneering resin composite or resin composite luting cement.<sup>37</sup>

Methods described above are only rarely, if ever, used in dental laboratories since they are not reliably applicable to all alloys. Moreover, newer technologies such as tribochemical silica-coating have gained popularity.

#### Pyrochemical Silica-coating

Pyrochemical silica-coating technologies are based on the use of elevated temperatures.<sup>38</sup> Such systems as Silicoater<sup>TM</sup> Classic, Silicoater<sup>TM</sup> MD, and Siloc<sup>TM</sup> (Heraeus-Kulzer, Wehrheim, Germany) have been used in dental laboratories for the fabrication of veneered metallic fixed partial dentures and metal frameworks for removable partial dentures since 1984.<sup>34</sup> The substrates are typically noble alloys, such as gold-silver-indium-palladium (Au-Ag-In-Pd) or base metal alloy such as cobalt-chromium (Co-Cr).

The Silicoater<sup>TM</sup> apparatus consists of a carousel on which the sandblasted casting passes through a special flame. The so-called coating solution is injected into the flame and results in a pyrochemical silica-coating of approximately 0.1-1.0  $\mu\text{m}$  thickness.<sup>39</sup> The coating solution contains tetraethoxysilane (TEOS), and the main chemical reaction in simplified form can be written as:



Treatment time and distance may vary in this technique. When the vaporized reactive silane fragments,  $-\text{Si}(\text{OH})_x\text{-C}$  (where  $x = 1, 2, 3$ ), reach the metal surface and are condensed onto the surface and the formed silica becomes embedded, the temperature is approximately 150-200°C. When the silica-coated surface has cooled to room temperature, it is silanized with a silane coupling agent. The silica-layer is about 50-80 nm thick prior to silanization.<sup>40</sup> After the recommended silane drying and reaction time of about 5 min, an opaquer (a dimethacrylate containing pigments) is applied and light-cured. Finally the veneering resin, which is also light-cured, is built up on the casting. This treatment is recommended due to enhanced bond strengths for resin composite inlays prior to cementation.<sup>41</sup>

Silicoater™ MD and Siloc™ are based on a colloidal silica and chromium trioxide application at an elevated temperature of 320°C.<sup>37</sup> In one study Silicoater™ Classic was applied to cobalt-chromium alloy cast clasps then veneered with tooth colored resin composites. It was observed the sandblasting did not weaken the clasps after bending tests.<sup>42</sup> However, it must be concluded Silicoater™ MD and Siloc™ techniques are less commonly used today since newer techniques were subsequently introduced.

A few years ago a modification of the Silicoater™ technology concept was introduced. It employed the extra-oral use of a compact hand-piece, commercially named Silano Pen™ or more recently, PyroSil Pen™ (Bredent, Senden, Germany).<sup>38</sup> It follows the same physico-chemical principles and mode of use as the Silicoater™ but is designed also for all-ceramics.<sup>43</sup> However, since there are no reported results of the long-term clinical experience of PyroSil Pen™ there is little more to be presented at this point in time.

### Grit-blasting Methods

It is obvious abrasion and roughening of a surface with a bur is inconsistent and arbitrary. A suitable treatment with many industrial applications on material surfaces is grit-blasting.<sup>44</sup> An observation from this overview of the current literature is



Grit-blasting

the terms 'sandblasting,' 'grit-blasting,' 'silica-coating,' 'roughening,' and 'air-borne particle abrasion' are sometimes used inconsistently in the dental materials literature. This could lead to misunderstanding and misinterpretation if the reader does not carefully distinguish the differences between these terms. For instance, grit-blasting is defined as an erosion procedure whereby the abrasive, such as silica or alumina ( $\text{Al}_2\text{O}_3$ ) sand, is delivered to the substrate suspended in or propelled by a stream of fluid.<sup>45</sup>

Grit-blasting or sandblasting cleans any greasy substance and creates micromechanical bonding and oxide layers to metal surfaces. In dental laboratories the procedure can be carried out by using glass beads and/or alumina sand, so-called "corundum particles" with a typical particle size of 50  $\mu\text{m}$  in diameter. Other typical working parameters are a nozzle distance of 10 mm and perpendicular to the surface and an application time of 10-15 seconds using an air pressure of 380 kPa.<sup>46</sup> When one thinks of the surface chemistry and chemical bonds formed at the interface, it must be noted if alumina gets embedded to the substrate it provides hydrolytically unstable  $-\text{Al}-\text{O}-\text{Si}-$  bonds which are weaker than  $-\text{Si}-\text{O}-\text{Si}-$  bonds.<sup>47</sup>

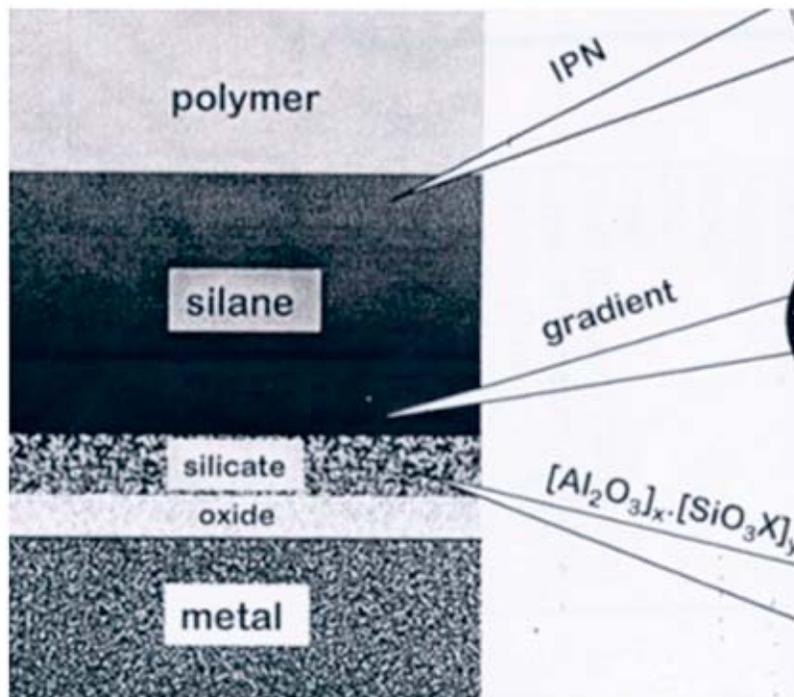
### Tribochemical Silica-coating and Silanization

Probably the most widely used silica-coating system is the tribochemical Rocatec™ System, introduced by ESPE (Seefeld, Germany) in 1989.<sup>29</sup> Silicatization is a specially engineered grit-blasting system based on special chemically designed silica-coated alumina particles for extra-oral conditioning



Tribochemical Silica-coating

of the substrate surface. This method can increase the bond strength due to the significant increase in silica content of the substrate surface.<sup>48</sup> Silicatization provides a chemical basis for silanes to enhance resin composite bonding since a silica-rich surface is needed for silanization in order to form strong  $-\text{Si}-\text{O}-\text{Si}-\text{C}-$  linking by silanes to the organic matrix.<sup>29</sup> Chair side versions for the dental office include such systems as Rocatector™ and CoJet™ (ESPE, Seefeld, Germany).<sup>49,50</sup>



**Figure 4.** Silanized silica-coated surface and siloxane film: interpenetrating polymer network (IPN) and the gradient model.  
(Courtesy of Professor Wim van Ooij, University of Cincinnati, OH, USA, 2001)

The first step in the tribochemical surface conditioning technique is surface blasting with airborne silica-coated alumina particles accelerated with compressed air. The silica-coated alumina particles impact the casting surface, and the resultant heat can reach up to 1200°C. This rapid momentary rise in the temperature is caused by the transfer of kinetic energy to heat energy.<sup>29</sup> The silica layer formed during this process is immediately embedded into the substrate surface. The gradient layer structure of a silanized silica-coated titanium surface can be modeled as presented in Figure 4.

Silicization also provides micromechanical retention for the resin.<sup>6</sup> In clinical conditions the silane is applied by brushing two or three drops of silane onto the silicized metal substrate. The silane is then gently air-dried before resin composite application.<sup>29</sup>

The use of silane coupling agents is a crucial ingredient for enhanced clinical success in creating long-term bonds of resin-to-metal<sup>51</sup> or resin-to-ceramic bonds.<sup>6</sup> *In vitro* experiments

have shown an increase of the shear bond strength between polymethylmethacrylate (PMMA) and the cast alloy as a result.<sup>52</sup> Recent studies suggested the tribochemical silica-coating method provides improvement in composite resin luting cement to non-etchable aluminum trioxide or zirconium dioxide ceramics.<sup>53</sup> This system also allows the bond of resin composite for the repair of existing resin composite restorations.<sup>54</sup>

### Experience with Base Metal and Noble Alloys, Titanium, and Steel

#### Different Alloys

The most frequently used base metal alloys in prosthetic dentistry are nickel, chromium, or cobalt alloys. The surface of chromium metal or its alloys are passivated spontaneously in air by an invisible thin chromium oxide layer that does not dull the surface finish.<sup>3</sup>

In a study of cobalt-chromium (Co-Cr) alloys the combination of thermal cycling and water storage of test samples has been recommended for improving the determination of the tensile

bond strength.<sup>55</sup> In these tests different adhesive systems such as silica-coating systems combined with silanization resulted in a substantial increase in the bond strength of the non-adhesive bis-GMA composite to Co-Cr alloy compared to sandblasting with alumina. Shear bond strength results were somewhat higher than results reported earlier.<sup>29</sup>

It has been claimed hydrolyzed silanol groups of silane have a better orientation towards Ni-Cr alloy sample surfaces resulting in more bonding sites for silanol groups on the alloy surface compared with high-palladium and gold-palladium alloy surfaces.<sup>56</sup> Nevertheless, it is important to note standardized grit-blasting methods have resulted in a higher volume loss for softer noble alloys than for base metal alloys. This was the conclusion of a study where morphology, surface composition changes, and volume loss of the substrate were evaluated for Co-Cr, nickel-chromium (Ni-Cr), and gold-silver-copper (Au-Ag-Cu) alloys.<sup>57</sup> It was also concluded ultrasonic cleaning of grit-blasted alloy surfaces silica-coated and silanized may improve resin bonding as loose blasting particles are removed. Also, three Rocatec™ system versions, Rocatec™ Pre and Rocatec™ Plus, have performed differently in alloy surfaces according to a scanning electron microscopy analysis.<sup>57</sup> Some noble alloys were silica-coated *in vitro* by CoJet™ chair side system, followed by silanization. This resulted in significantly higher adhesion results to resin composite on those alloys.<sup>50</sup> A recent study confirmed the efficacy of adhesion when a resin composite was bonded to silanized substrates such as gold-palladium-platinum (Au-Pd-Pt) alloys and feldspathic porcelain when treated using abrasion with alumina particles (Rocatec™ Pre) followed by an impact silica-coating (Rocatec™ Plus) and silanization with a silane coupling agent. However, the corresponding Weibull modulus values were low, suggesting inconsistency in the reliability of the bond strengths.<sup>58</sup>

All the base metal and noble alloys described and cited above are in continuous clinical use. For those interested in gold and in particular heat-treatment of gold alloys, the technique is described elsewhere.<sup>59</sup>

## Titanium

Titanium and its alloys have gained much interest in biomedicine as a biomaterial and is usually formally classified as a noble metal due to its superior biocompatibility properties and non-cytotoxicity.<sup>60</sup> Through a chemical process an extremely thin corrosion-resistant oxide layer forms on its surface inhibiting further corrosion and facilitating its compatibility with living tissues.<sup>61</sup> Titanium is a commonly used metal in dentistry for dental implants, crowns, and for CAD/CAM-milled implant substructures veneered with a particulate filled resin composite.<sup>62</sup> The adhesion of methacrylate-based polymers to titanium with the coupling agent MPS has been evaluated. Long-term storage in water at 37°C significantly reduced bond strengths. Moreover, the adhesion between the polymer and titanium was found to be of a chemical nature.<sup>63</sup> Silica-coating with a pyrochemical Silicoater™ or tribochemical Rocatec™ system provided different thicknesses for silica-coating layers on the titanium substrate. When analyzed statistically, the silica contents derived from the two coating systems did not differ. Also, the volume loss of titanium in the Rocatec™ process was comparable to those observations with base metal alloys, but it was not shown to be critical to the clinical fit of the restoration.<sup>64</sup>

Some less investigated silane coupling agents have been recently evaluated *in vitro*: activated dilute 3-isocyanatopropyltriethoxysilane<sup>65</sup> (Figure 5) and 3-acryloyloxypropyltrimethoxysilane<sup>66</sup> (Figure 6) solutions proved to have a role on the adhesion promotion bonding *bis*-GMA resins to silica-coated titanium.

On the other hand, according to some recent research results, titanium without silica-coating has shown some adhesion to a veneering resin composite when silanized with MPS and two less common silanes (Figures 7 and 8).<sup>67</sup>

## Steel

Silanized smooth stainless steel rods have been evaluated and investigated as a potential dental material in an acrylic resin, PMMA matrix. Immersion in water reduced the strength of the bond between silane-treated rods and polymerized resin, but the strength was increased with age when the specimens were left in air.<sup>68</sup>

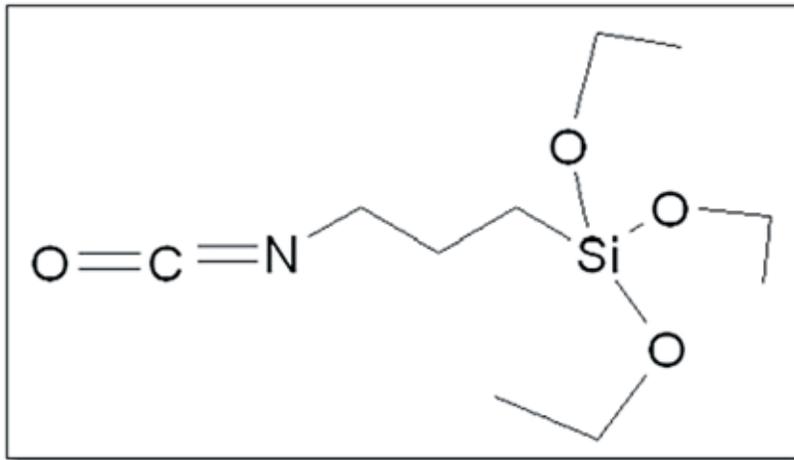


Figure 5. The 3-isocyanatopropyltriethoxysilane coupling agent.

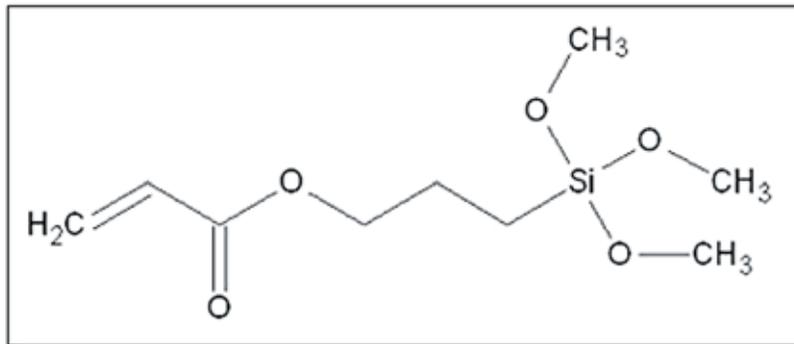


Figure 6. The 3-acryloyloxypropyltrimethoxysilane coupling agent.

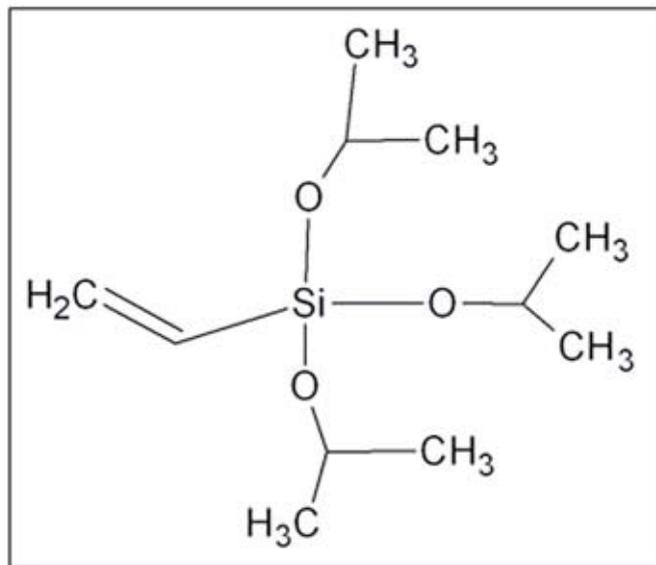
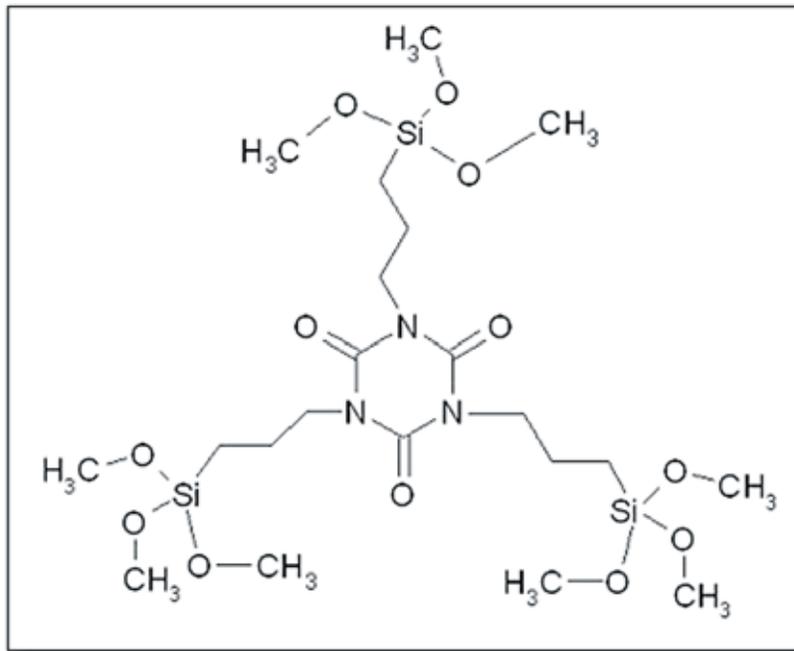


Figure 7. The vinyltriisopropoxysilane coupling agent.



**Figure 8.** The tris-(3-methoxysilylpropyl) isocyanurate coupling agent.

### Conclusions

1. Tribochemical silica-coating (silicatization) is widely used today in dental laboratories and in the dental office for bonding resin composites to base metal and noble metal alloys, ceramics, and composites. It provides reliable bonding when the silica-coated substrate is immediately silanized. Silanization is mandatory to achieve success.
2. Other silica-coating methods such as pyrochemical are seldom applied in practical dental laboratory work today.
3. It can be noted a great number of silane-related clinical or research based studies have been published in dentistry. However, there is a lack of clinically proven information on the function of silanes other than MPS as an adhesion promoter for dental materials.

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