Silanes and inorganic particles

The winning combination for scratch and abrasion resistant coatings.

Björn Borup, Roland Edelmann, Reiner Mehnert

Requirements on surface material are especially exigent in wooden floorings. In an effort to introduce a coating with a new level of use resistance, a new system based on inorganic nanoparticles and silanes is presented. Silane technology allows for the incorporation of up to 30% (w/w) fumed silica in an acrylic resin. This leads to solvent free, UV- or electron beam cured coatings with an increased scratch and abrasion resistance.

Design considerations in general

In devising a new system desirable features, such as ease of use and environmental considerations, can be included in the design. Thus, it is essential that a system has no volatile organic components (VOC) and still exceeds the current performance standards. Furthermore, application of the coating should be possible with easily available equipment. The system is designed to have the following benefits for the user:
- 100% reactive
- No solvent (VOC-free)
- High inorganic content
- Rapid curing (few tenths of a second) due to UV-technology/electron beam technology
- Application via roll coating
- Intimate interconnection of organic and inorganic components
- Exceeds current performance standards in parquet coating technology

Components

Given the enormous breadth of specifications in the flooring industry, even for parquet, a number of different compositions are needed to satisfy these demands. A rough guide on what major components comprise the system:
- Silane 10 - 15%
- Fumed silica 15 - 25%
- Acrylic resin 50 - 70%
- Corundum microparticles 0 - 15%

Identity and amounts of the individual components will depend on the demands of the individual coating. For example sandable parquet flooring will not contain any corundum. The other components will depend on the gloss, transparency, and stain resistance required. Fumed silica, silanes, and their interaction will be described in order to better understand how this new technology provides for optimal performance.

Fumed silica

Fumed silica, a highly dispersed, amorphous silica, is composed of aggregates that are agglomerated. These agglomerates can be decomposed by normal dispersion processes in coatings to aggregates (deaggregation is usually not possible by dispersion in coatings). These aggregates are composed of almost spherical primary particles that are of nanometer size (on the order of approx. 5-50 nm). Fumed silica is characterized by a large surface area (approx. 50 - 600 m²/g) that is covered with Si-OH groups (figure 1a). This is crucial to this technology. Fumed silica is a common ingredient in coating formulations and can act, for instance, as a suspension agent, pigment-stabilizer, and rheology control agent (either as thickener or thixotropic agent). Special types of fumed silica are appropriate for each of these applications and are added in amounts of a few percent (at most).

In order to obtain scratch resistance fumed silica needs to be added in amounts of 20% (w/w) or more. The incorporation of such a large amount of fumed silica, without increasing the viscosity above levels that are acceptable, is only possible with the help of silanes.

Organofunctional silanes

Organofunctional silanes are bifunctional molecules (figure 1b) and have an organofunctional group (Y or vinyl group) and a silicon-functional (or inorganic) part (OR), usually consisting of ethoxy or methoxy groups (other groups such as acetoxy, propoxy etc. are also possible). These two groups react in completely different but complementary ways and give the silanes their particular properties.

Hydrolysis activates the alkoxy groups of the silane (figure 1c). The in figure 1c described reaction of the alkoxide (Si-OR) group to form a hydroxyl (Si-OH) group can be extended to the other two alkoxide groups on the molecule, as usually all three alkoxide groups are reactive.

Subsequently, a Si-OH group reacts with the hydroxyl group of an inorganic substrate (figure 1d) to form a chemical bond between the silane and the inorganic substrate. A second chemical bond is formed between the binder and the silane through the (Y) organofunctional group. It is important to choose the organofunctional group (Y or vinyl group see figure 1b) for compatibility with the binder system. This reactivity of the silane with an inorganic substrate can be extended to inorganic fillers, pigments, and other inorganic particles such as fumed silica as well. In generally, it can be said that potential applications for silanes result from the bifunctionality of this class of compounds.

Synthesis of the UV-cured coating material

For the synthesis of the UV-cured system a large amount (vide supra) of fumed silica has to be introduced into the acrylic resin without that an inordinate increase in the viscosity occurs. For this purpose the acrylate is heated to approximately 60 °C upon which the silane, a stoichiometric amount of water, and a catalyst is added. Into this mixture the fumed silica is introduced under extensive dispersion. This introduction of the fumed silica under reaction with the silane is an essential part of the technology. Simple addition of silane to an acryl suspension of fumed silica does not lead to low viscosity formulations.

During this dispersion process the silane reacts with the surface of the fumed silica. It is the deliberate covering of the fumed silica with a siloxane shell that leads to these low viscosity systems (figure 2).

A model of the reaction of the silane with the hydroxyl rich surface of the fumed silica is given in figure 3 (see also figure 1d). Further reaction (condensation) of more silane molecules with the surface of the fumed silica and the already attached silane molecules results in the described (figure 2) siloxane shell. This shell covers the hydrophilic hydroxyl groups of the fumed silica giving it a hydrophobic and organofunctional outer shell, compatible with organic resins.

Reaction of the silane with the aggregated fumed silica occurs within the acrylate resin, resulting in a certain degree of deagglomeration. Primary particles (as implicated by figure 3) are usually not observed.

Performance of UV-cured hybrid systems

As this system is relatively new, the relationship between the content of fumed silica and the scratch resistance was...
investigated to see how they correlate. Similarly, considering the importance of abrasion resistance, the effect of corundum microparticles in the system was investigated.

**Scratch resistance**
In order to obtain a scratch resistant coating it is of utmost importance to increase the inorganic content to about 20% or more, as the scratch resistance improves markedly above this content. To demonstrate this relationship (figure 4) several different amounts of fumed silica were dispersed in a polyester acrylate ("Viaklin VTE 5968") using the described technology. The adhesion resistance of this system was tested by gravimetric determination (after 50 cycles) using the Taber-Abraser CS 0/5 4/N (EN 438:2/6). The scratch resistance was tested by haze after 100 cycles CS 10/5:4/N (EN 438:2/7).

In general, if this new coating system can be applied to the surface of the substrate (be it paper, metal or plastic) using roll or spray coating upon which it is UV- (or electron beam) cured, a process which takes less than a second. The resulting coatings are clear and can have varying degrees of scratch and abrasion resistance, depending on the particular formulation. Representative test results on decorative paper of the modified and unmodified polyester acrylate are given in table 1.

**Abrasiveness resistance**
Several different levels of abrasion resistance can be attained with this new system, depending on the exact formulation and the demand of the application. One of the most demanding applications in this regard is flooring. The technology presented here allows for the incorporation of corundum particles into this newly presented coating system.

Improvements in the abrasion resistance obtainable by these systems is enormous. Figure 6 demonstrates the difference in abrasion resistance obtainable with corundum. Sample A (unmodified acrylic coating) was exposed to 250 cycles of a Taber-Abraser CS 17 (5.4 N) and shows significant wear. Sample B (same acrylic coating modified with fumed silica, silane, and corundum) exposed to 750 cycles of the same Taber-Abraser shows only a small shadow where abrasive action had taken place.

**Performance of the UV-cured coating as parquet flooring**
When the coating system is applied as a top coat on a parquet floorboard it serves as a protective and abrasion resistant surface. In these experiments a typical wooden parquet technology was used, where already a resistant coating was applied on the seal coat of a pretreated parquet panel. A simple procedure to produce matte coatings without the addition of matting agents. Shrinkage of the cured layer causes some surface structuring which results in a matte appearance of the coated surface, a simple procedure to produce matte coatings without the addition of matting agents.

Using this lab unit an acrylate-nanocomposite top coat was applied on the seal coat of a pretreated parquet panel. A depth profile taken after Taber abrasion shows that the thickness of the top coat is about 25 µm (figure 8). Taber abrasion was done according to the standard EN 438:2/6 (S 42/5.4 N). From the number of cycles needed to abrade through the depth of the top layer the specific abrasion was determined to be 15 cycles/µm, a typical value for nanocomposite coatings that do not contain corundum. Much higher values can be obtained with corundum containing nanocomposites which can reach specific abrasions of 35 - 40 cycles/µm (table 2).

**References**
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Results at a glance
- Coatings containing up to 20% or more of fumed silica can be designed and produced with relatively low viscosity.
- These kinds of coatings have an excellent scratch resistance.
- Incorporation of corundum into the formulation of the system improves markedly the already excellent abrasion resistance.

This paper was previously presented at the Parquet Coatings Conference in Berlin.

The authors:
-> Roland Edelmann studied color chemistry at the Technical University of Dresden in Germany. From 1969 to 1991 he worked in the areas of research, technical service, and production at the silicone producer Nünchritz. From 1991 he has been responsible for technical service (since 1996 also R&D) silanes and silicic acid esters for coatings and foundry resins at the company Degussa.
-> Prof. Dr. Reiner Mehnert, physicist, is professor at the University of Leipzig (Germany). For more than 20 years he has been working on electron beam and UV-curing technologies. As head of department at the Institute for Surface Modification (IOM) he is responsible for research and development in the field of polyacrylate nanocomposites.
-> Dr. Björn Borup obtained his doctorate in inorganic chemistry from Indiana University (Bloomington). In 1998 he joined the former Sivento GmbH (now part of Degussa) where he was involved research on sol-gel materials for coatings and dental materials. Since 2000 he has been responsible for R&D and technical service silanes for coatings and foundry resins.
Figure 1: a) Surface functionality of a fumed silica particle
Figure 1: b) Silanes are bifunctional molecules
Figure 1: c) Hydrolysis reaction of a organofunctional silane
Figure 1: d) Condensation of an organofunctional silane with an inorganic substrate
Figure 2: Siloxane shell covering the inorganic particle.
Figure 3: Model reaction of silane with fumed silica to form a siloxane shell
Figure 4: Scratch and abrasion resistance of the hybrid coating
Figure 6: Difference in scratch resistance for a unmodified and an inorganically modified acrylate system.
Figure 8: Depth profile of the nanocomposite coatings applied to a sample parquet floorboard
Figure 8: Depth profile of the nanocomposite coatings applied to a sample parquet floorboard.
### Table 1: Scratch resistance of hybrid coating using a number of methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Taber-Abraser CS 0/S42 [mg]</th>
<th>Erichsen Scratch Resistance [N]</th>
<th>Haze [%] **)</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viaktin VTE 5968</td>
<td>67.7</td>
<td>0.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Modified System</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viaktin VTE 5968*)</td>
<td>20.2</td>
<td>3.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

*) Containing approx. 28% fumed silica, 14% Silane, 58% Viaktin VTE 5968

**) Taber-Abraser CS-10/5.4 N
Table 2: Comparison of a standard parquet coating to a nanocomposite coating

<table>
<thead>
<tr>
<th>Coating Properties</th>
<th>Nanocomposite</th>
<th>Representative</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 layer</td>
<td>2 layers</td>
</tr>
<tr>
<td>Clarity</td>
<td>good</td>
<td>slightly cloudy milky</td>
</tr>
<tr>
<td>Coating Thickness/µm</td>
<td>35</td>
<td>75</td>
</tr>
<tr>
<td>Steel wool scratch</td>
<td>Fine</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>Coarse</td>
<td>Pass</td>
</tr>
<tr>
<td>Gloss retention</td>
<td>75 cys</td>
<td>101 %</td>
</tr>
<tr>
<td>Taber Abrasion 542/cps</td>
<td>225 cys</td>
<td>96 %</td>
</tr>
<tr>
<td>Taber Abrasion 542/cps</td>
<td>1400</td>
<td>2600</td>
</tr>
<tr>
<td>Stain resistance</td>
<td>Shoe polish</td>
<td>pass</td>
</tr>
<tr>
<td></td>
<td>Iodine</td>
<td>pass</td>
</tr>
<tr>
<td></td>
<td>Asphalt</td>
<td>pass</td>
</tr>
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