



The best of two worlds

Silane-urethane hybrid crosslinkers create scratch-resistant clearcoats

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A range of silane-urethane hybrid crosslinkers has been designed to generate multifunctional, scratch resistant coatings usable on a variety of substrates. Addition of one such product to a 2K polyurethane automotive clearcoat greatly increased scratch resistance. An ambient-cure clearcoat applied over wood as well as plastic also showed very high scratch resistance.

A new and versatile product family of crosslinkers and binders for high performance coatings has been developed. The novel approach combines the benefits of silane chemistry with the performance of polyurethanes, providing excellent scratch resistance while maintaining urethane properties in coatings. 3-isocyanatopropyltrimethoxysilane (IPMS) is the core building block of the novel technology platform and provides a broad freedom of design by creating tailor-made binders and crosslinkers. This resin concept also enables non-isocyanate (NISO) crosslinking technology that matches or exceeds polyurethane performance.

Modern aliphatic 2K polyurethane clearcoats are considered as today's benchmark for environmental etch, weathering and durability. They are in general well known for their excellent balance of flexibility and hardness. Furthermore, superb overall properties and good adhesion to various substrates are advantages which have helped the technology to set the benchmark in clearcoats for the automotive industry in recent decades. Here, the automobile topcoat in particular, which is crucial to a car's visual appearance, needs to have several properties each at the highest level to satisfy the premium requirements of the car manufacturers and their customers.

Clearcoats need to meet very high requirements

The clearcoat layer of a car (approximately 40 µm thick) is its first defence barrier against all kinds of mechanical, physical and chemical influences and thus has to resist many attacks – whether by UV radiation, abrasion caused by car wash brushes and dust, leaving micro-scratches, or aggressive chemicals such as acidic rain or suntan lotion causing swelling and discolouration (haze).

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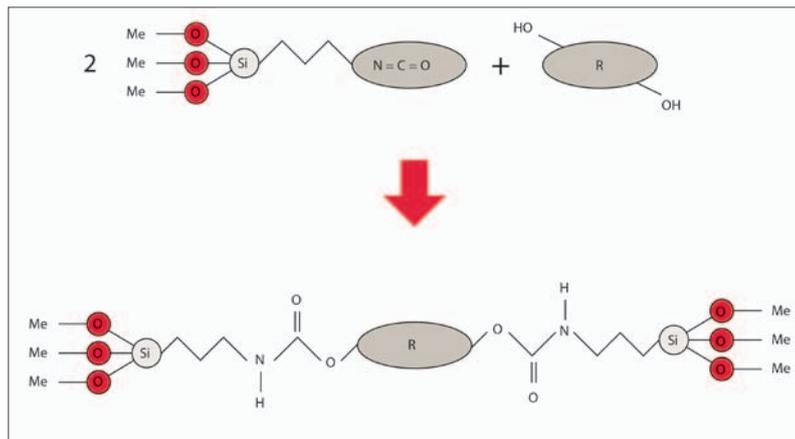


Figure 1: IPMS-based silane-urethane hybrid crosslinker containing urethane groups, terminated by tri-functional alkoxy-silane structures

The clearcoat needs to remain shiny, glossy and transparent for as long as possible – even after years it should still look like new. The quality of clearcoats has steadily improved, but nevertheless there is still a need to significantly improve certain characteristics – particularly the scratch resistance – while also if possible adding more features such as an easy-to-clean effect [1]. This trend is not just limited to automotive clearcoats. It is also true for ambient temperature curable clearcoats applied on other substrates such as wood or plastic, which are more heat sensitive.

Crosslinking of silane-urethane systems outlined

An appropriate way to gain reliable enhancements, in increasing the scratch resistances of clearcoats and to satisfy market needs and trends concerning a further integration of functions, is ensured by the use of silane-urethane hybrid crosslinkers.

As shown in Figure 1, the IPMS that represents the key building block of the system can be converted with any kind of isocyanate-reactive groups (R-group) preferably with the hydroxyl groups of diols, polyols or oligomeric diols to build a urethane linked but alkoxy-silane functional non-isocyanate (NISO) crosslinker/binder.

The choice of R-group will primarily determine the properties of the crosslinker and hence will also significantly influence the attributes of the coating. For example, the longer the backbone of the crosslinker the more it acts as a flexibiliser in the coating. In contrast, a branched and short R-group will result in higher hardness. It is also possible in principle to use diols with additional functionalities incorporated, such as fluorinated compounds, to create coatings which are even more multifunctional. But due to the fact that the urethane linkages are imparted by formulating with IPMS-based crosslinkers, the beneficial properties which are expected from aliphatic polyurethanes such as high chemical resistance, good adhesion and excellent mechanical properties, are retained.

There are two possible reaction mechanisms by which the IPMS-based crosslinkers shown can react via their alkoxy groups in coating systems. One reaction is a combination of hydrolysis and condensation to form siloxane

linkages (Si-O-Si). The other crosslinking mechanism is a transesterification reaction which occurs only if a hydroxyl group, for example that of an acrylic or other polyol, is present. Each of these mechanisms can be accelerated by using appropriate catalysts which are extensively described in diverse publications [2, 3].

This paper describes a performance analysis of coatings which have been crosslinked using unique alkoxy-silane terminated crosslinkers which contain urethane structures within their backbone. The paper focuses on systems which facilitate the self-crosslinking mechanism of the alkoxy functionalities (Figure 2).

The new silane-urethane hybrid crosslinkers were used both in standard OEM-clearcoat 2K PUR formulations and in 1K self-crosslinking, moisture-cure systems.

Test procedures summarised

To analyse the impact of siloxane networks in standard 2K PUR systems, clearcoats were formulated using an acrylic polyol, an HDI-trimer (hexamethylene diisocyanate) “Vestanat HT 2500 L” (PUR-hardener, NCO:OH ratio 1:1) and several levels of the silane-urethane hybrid crosslinker “Vestanat EP-M 95” (crosslinker M 95, low viscosity liquid, 100 % solids) where the R-group is a short chain, linear aliphatic diol. Also, to accelerate the crosslinking of the alkoxy groups a catalyst “Vestanat EP-CAT 11” (Cat 11, alkyl ammonium salt) was added [4].

The clearcoat concept based on these products is shown in Figure 3. To provide a broader understanding of the influence of siloxane networks on the resulting coating properties, the dosage of crosslinker M 95 was varied. In

Results at a glance

- »» The “Vestanat EP-M” range is a family of silane-urethane hybrid crosslinkers designed to generate multifunctional, scratch resistant coatings usable on a variety of substrates. Some will cure even at ambient temperature.
- »» These crosslinkers and binders can be used in automotive OEM and refinish applications and on many different substrates such as wood, plastic and metals or glass etc.
- »» Incorporation of these products into an existing 2K polyurethane clearcoat formulation had little effect on most physical properties but produced a considerable increase in scratch resistance. High levels of scratch resistance were also obtained on an ambient-cure clearcoat applied over wood.
- »» Resistance to suntan lotion of automotive clearcoats could also be improved.
- »» Other modifications can also be incorporated, such as fluorine, which was shown to produce a more hydrophobic and oleophobic surface, leading to easy-to-clean properties.

the figure, the 50:50 pbw blend refers to the ratio of the solids of acrylic polyol plus PU crosslinker and the silane-urethane hybrid crosslinker. In other words, the hybrid crosslinker was added at the same amount (on solids) as the resin plus PUR hardener. The clearcoats were cured at 140 °C (oven temperature) for 22 minutes.

Scratch resistance shows significant improvement

The compatibility of the hybrid crosslinker with other formulation constituents was excellent in general. In all cases high gloss clearcoats were obtained (82 ± 2 gloss units at 20 °)

As shown in Table 1, all coatings based on the hybrid crosslinker show a well-balanced mechanical property profile which is satisfactory for many high end applications. When the concentration of hybrid crosslinker is increased, the hardness and flexibility of the clearcoat slightly decreases, while chemical resistance against sulfuric acid is maintained.

It becomes apparent that the typical polyurethane characteristics such as outstanding hardness combined with flexibility (reference system = 0 % dosage hybrid crosslinker) were only slightly diluted by the addition of the siloxane network. But even in the 100 % system the mechanical performance is still at an excellent level, as confirmed by the direct impact test.

The scratch resistance was tested by a modified crockmeter test (wet abrasion). The test performed consists of

Table 1: Properties of 2K PUR System modified with various amounts of Crosslinker M 95

Level of Crosslinker M 95	0 %	10 %	30 %	50 %	100 %
Hardness (König) 1 d	171	174	164	162	143
Erichsen cupping (mm)	8.0	8.5	7.0	6.0	7.0
Impact, direct (in-lb)	> 80	> 80	> 80	> 80	80
Acid etch (20 % H ₂ SO ₄), first impact/destroyed	47 °C / 65 °C	48 °C / 67 °C	44 °C / 62 °C	40 °C / 61 °C	46 °C / 71 °C
MEK resistance (double rubs)	> 150	> 150	> 150	> 150	> 150

a bar with an abrasive textile brushing the coated surface in a detergent solution 160 times with a 2 kg weight attached to it to provide sufficient force. After this test, the gloss is measured again and the residual gloss is calculated in percent. This test is similar to scratch tests for automotive OEM requirements [5].

The resistance against scratching increases dramatically with the addition of hybrid crosslinker. Figure 4 shows that even small proportions of approximately 10 % show a significant effect. The residual gloss after the modified crockmeter test was significantly higher compared to the reference system (0 % dosage hybrid crosslinker).

The scratch resistance differences of the formulations can be measured but they are also easily visually detectable (Figure 5).

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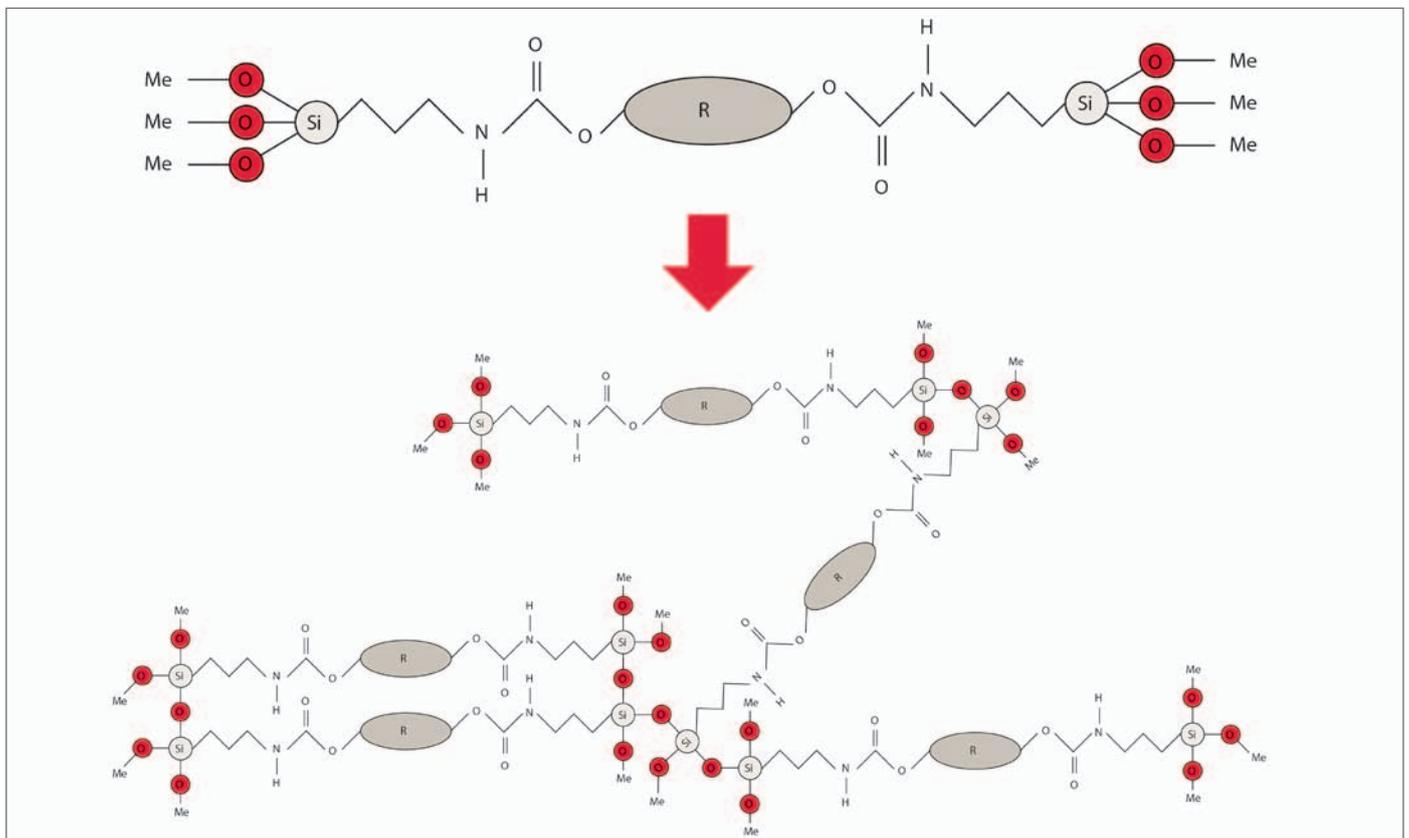


Figure 2: Hydrolysis-condensation reaction forming siloxane networks

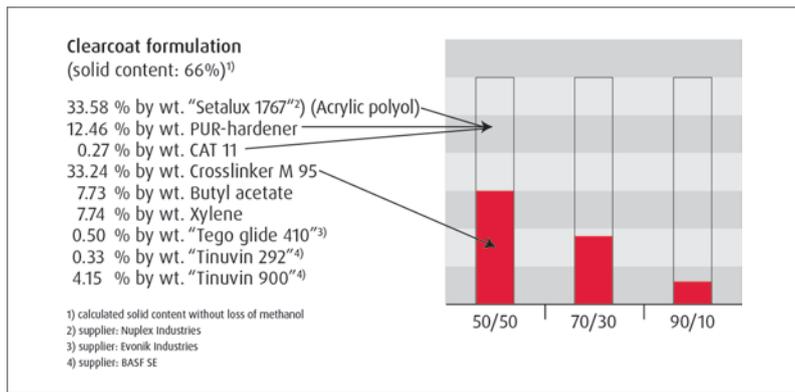


Figure 3: Example of a clearcoat formulation with 50:50 pbw (on solids) of resin/PUR-hardener and crosslinker M 95

Resistance to suntan lotion can also be improved

The "100 %" formulation was also investigated in relation to other aspects of chemical resistance. Resistance against suntan lotion is known to be very relevant for automotive interior coatings but recently this has also become relevant for automotive exterior clearcoats. The clearcoat formulation based on the 100 % dosage of hybrid crosslinker was compared with a 2K PUR system with regard to resistance against an SPF 30 suntan lotion in a temperature gradient oven test for 30 minutes. While the standard 2K PUR coating shows swelling and discolouration (Figure 6) even at 37 °C, the boosted formulation with 100 % hybrid crosslinker remains stable even at higher temperatures up to 55 °C. The better resistance against suntan lotion can be explained by an increase in crosslink density via the dense siloxane network [5, 6].

Silane-urethane hybrids for moisture curing systems

Even in ambient curing systems, special silane-urethane hybrid products can act as a crosslinker as well as a binder at the same time to create multifunctional scratch-resistant coatings. In the field of wood coatings in particular, the drying speed of the coating is an essential factor. For this special purpose the "Vestanat EP-MF" product family was designed based on products of the "Vestanat M" family but designed to be curable at room temperature (See Figure 7).

"Vestanat EP-MF 201" (crosslinker MF 201) is a solvent and isocyanate free, ready-to-use version of an alkoxy-silane terminated crosslinker or binder requiring no other crosslinkers (i.e. polyisocyanates). It can be used for 1K moisture curing systems. The resulting coatings show outstanding scratch, stain and chemical resistance.

2K formulations are obtained by combining the silane-terminated product with polyols. The right mixing ratio between both components must then be determined. Due to the formation of an interpenetrated network, properties including scratch, stain and chemical resistance can be adjusted on demand. There is also no need to add polyisocyanate crosslinkers. The final coating is still a NISO system and – depending on the characteristics of the polyol – potentially low in VOC.

Figure 8 shows a technology comparison between a 2K PUR (left) and a 2K formulation based on use of the silane-terminated crosslinker-binder (right). Both systems were applied on wood and were scratched using a modified crockmeter test. While many and very distinctive scratches occur on the unmodified 2K PUR, the formulation based on silane crosslinking resists the abrasive attacks keeping its shiny, initial appearance.

In addition to the field of wood coatings, there is also an attractive application in terms of plastic coatings. Here the same properties will lead to scratch, stain and chemical resistant coatings. This outstanding product profile is essential for sporting goods or in the automotive industry.

Figure 4: Residual gloss after modified scratch test of a 2K PUR system formulated with PUR-hardener and additional levels of crosslinker M 95

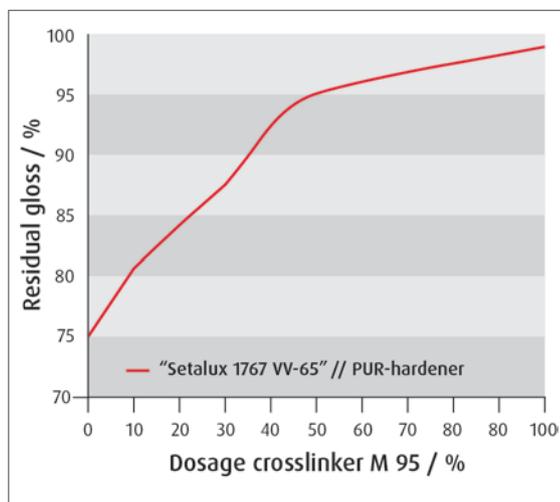


Figure 5: Modified crockmeter test: 2K PUR (left) vs. 2K PUR formulated with 100 % addition of hybrid crosslinker (right)

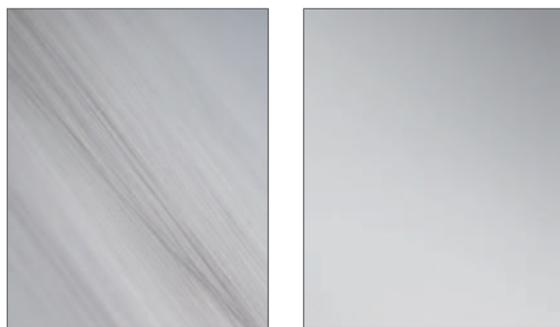
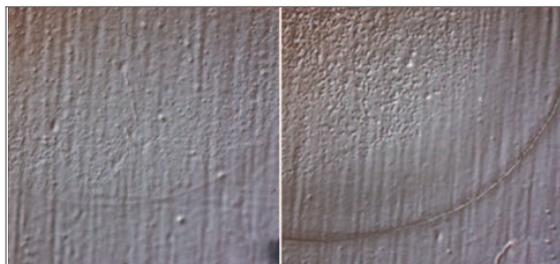


Figure 6: 2K PUR with additional dosages of crosslinker M 95 (left - less structured surface at 55 °C) vs. 2K PUR (right - highly structured surface due to less suntan resistance at 55 °C)



	Crosslinker MF 201	Crosslinker M 95
	0°C	80°C
	160°C	
Curing conditions	Ambient temperature	Thermal cure
Flexibilizer	"Vestanat EP-MF 202"*	"Vestanat EP-M 222"*
Crosslinking mechanism	1K Moisture cure 2K Transesterfication	Boost of 2K-PUR Transesterfication (acrylic polyols)
Applications	Wood, plastic, maintenance	Automotive, industrial

*Not discussed in the article

Figure 7: Silane-urethane-hybrid crosslinkers based on IPMS designed for creating multifunctional, scratch resistant coatings in different systems and curing conditions

Fluorine incorporation enhances cleanability

The backbone of the novel crosslinker technology is variable, which leads automatically to a high freedom of design for creating tailor-made crosslinkers or binder with multifunctional qualities in the future.

An experimental (not currently commercially available) fluorine-containing silane-urethane hybrid hardener was investigated. Fluorine is well known for its positive effects on surface properties, such as the improvement of water and oil repellency of coatings, also known as the easy-to-clean effect [7]. One indirect but valid method for detecting the hydrophobicity of surfaces is to measure the contact angle of a drop of liquid onto that surface. In this case water and squalene, a triterpene which can be obtained from shark liver oil, were used as liquids. Clearcoats were formulated both with the "Vestanat® EP-M 95" (reference) and with several levels of the experimental fluorine containing silane-urethane hybrid crosslinker. The coatings were cured at 140 °C (oven temperature) for 22 minutes.

The results obtained, shown in *Table 2*, demonstrate that even small proportions of a silane-urethane crosslinker containing fluorine can enhance the easy-to-clean behaviour of a coating significantly. It was also noted that all clearcoats tested had in general a high abrasion resistance. The only deficit observed was a continuing decrease of hydrophobicity after several scratch test cycles. ◀



Figure 8: Modified crockmeter scratch test : 2K PUR (left) vs. 2K based crosslinker MF 201 formulation (right)

Crosslinker M95 content	Fluorine crosslinker	Contact angle	
		Water	Squalene
100 %		94	33
95 %	5 %	109	72
85 %	15 %	113	72

Table 2: Easy-to-clean effect of silane-urethane hybrid crosslinkers containing fluorine

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