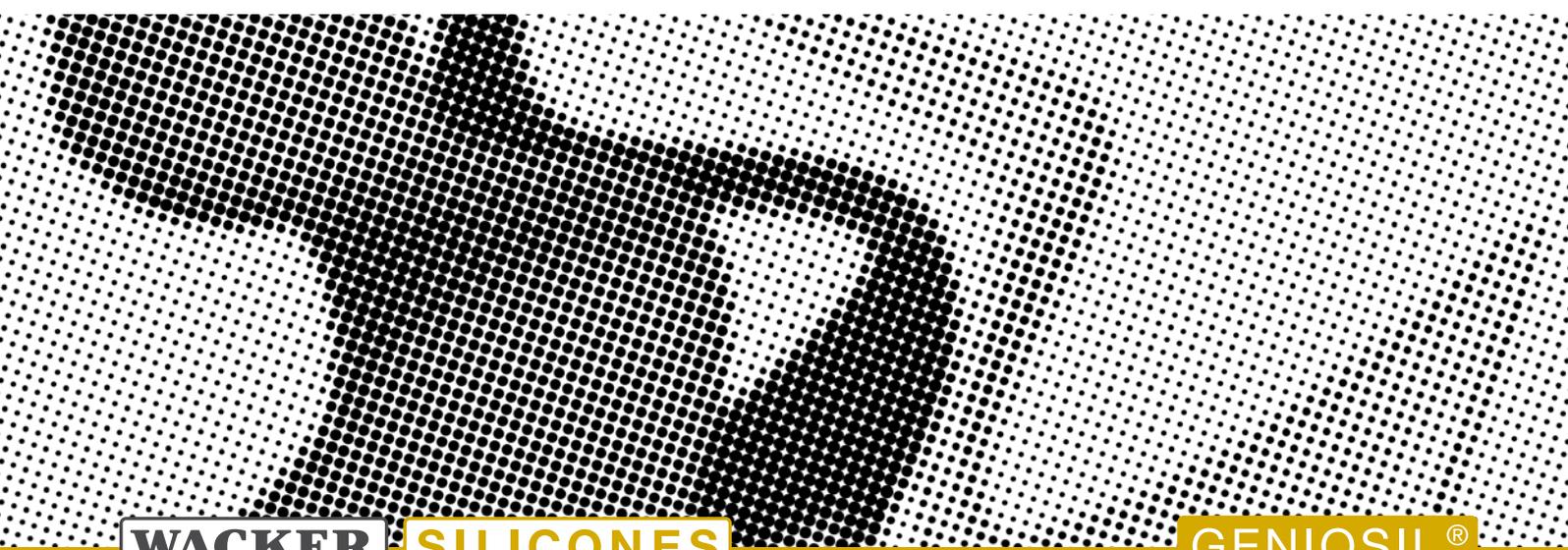


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WACKER **SILICONES**

GENIOSIL®

ALPHA SILANES – NEW BUILDING BLOCKS
FOR HIGH-PERFORMANCE COATINGS
PRESENTATION BY J. PFEIFFER
AT THE EUROPEAN COATINGS SHOW 2005

CREATING TOMORROW'S SOLUTIONS

ALPHA SILANES – NEW BUILDING BLOCKS FOR HIGH- PERFORMANCE COATINGS

Text: Dr. Jürgen Pfeiffer

1. Introduction

Organofunctional silanes have been used in various coating systems with great success for several decades now. By far the most decisive function is as an adhesion promoting agent between either an inorganic substrate and an organic coating or sometimes even between different organic substrates [1, 2]. In addition, organofunctional silanes can act as a crosslinking agent when introduced into a polymer backbone either during the polymer synthesis or via a polymer-analogous reaction. The crosslinking is effected by hydrolysis of the alkoxy silyl groups leading to silanol formation and subsequent condensation of these silanol groups to yield siloxane bridges between the polymer molecules (**Figure 1**).

As a result of the silane crosslinking, important properties such as chemical resistance, gloss, coefficient of friction, or mar resistance of the cured coating can often be significantly improved [3].

2. Organofunctional silanes with α -effect

Commercially available organofunctional silanes almost always have a propylene spacer linking the organofunctional group (e.g. amino, epoxy, methacryloyloxy) and the silane moiety. In addition, most products currently available bear three hydrolyzable groups (alkoxy groups in most cases), leading

to essentially rigid three-dimensional structures upon self-condensation. The reason for the focus on such silane structures that have a propylene spacer and trifunctionality can be found in the raw material source. These molecules are synthesized via readily available allyl building blocks (e.g. allyl chloride) and trichlorosilane. However, Müller-Rochow process chemistry is required as the raw material source where difunctional silanes are to be synthesized. Whereas standard organofunctional silanes lead to excellent product properties in many applications, there is a further need for a broader range of products to meet changing market requirements.

The main requirements still not met by the currently available organofunctional silanes are

- a broader range of alkoxy groups (which allows a variable hydrolysis speed)
- availability of difunctional silanes (making it possible to trigger crosslinking density and to reduce the amount of volatile organic compounds)

By changing the spacer from propylene to methylene, the reactivity of organofunctional silanes can alter dramatically, especially with respect to hydrolysis and condensation as shown above. This so-called “ α -effect” seems to be the result of an electron transfer from the organofunctional group to the silane group (**Figure 2**).

Fig. 1: Hydrolysis and condensation of alkoxy silyl groups

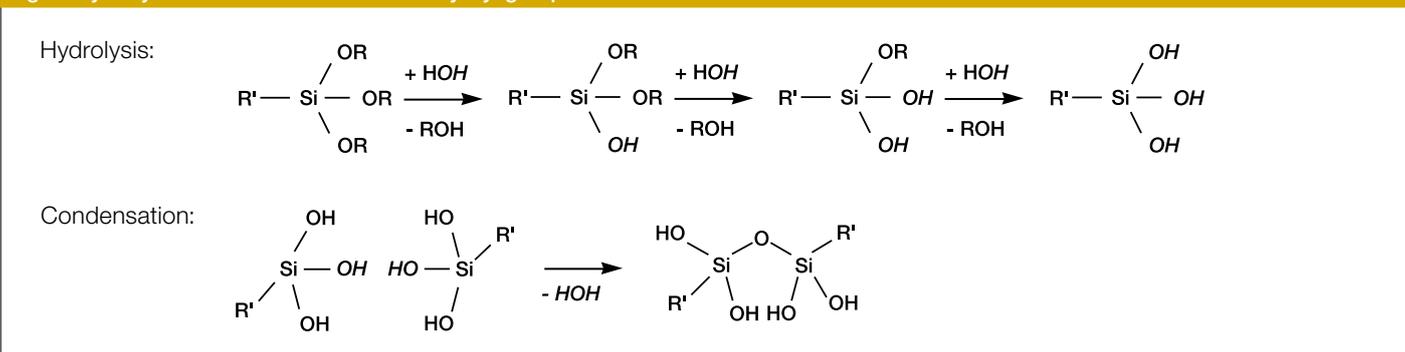


Fig. 2: The α -effect – activation of organofunctional silanes with methylene spacer



A broad range of these α -silanes has now been launched by WACKER SILICONES under the tradename GENIOSIL®* to make their benefits available to the market. Special production processes have been installed and several product groups bearing functionalities like methacryloyloxy, isocyanato, amino and carbamato are now available in commercial quantities.

The influence of the above mentioned spacer length on hydrolysis as well as on condensation behavior can be dramatic, as can be seen by comparing hydrolysis rates of various

methacryloyloxymethyl silanes with their standard counterpart GENIOSIL® GF 31 (Figure 3).

No conclusion can be drawn here as to reaction rates for condensation, which is certainly just as important as hydrolysis. Tests were conducted to obtain initial qualitative comparisons using organofunctional α -silanes and their γ -counterparts with respect to condensation. This involved end-capping of hydroxyterminated polyethers with isocyanate-functional silanes and determination of the tack-free time of resultant films (Figure 4).

Fig. 3: Hydrolysis rates of the first alkoxy group of several methacrylfunctional silanes

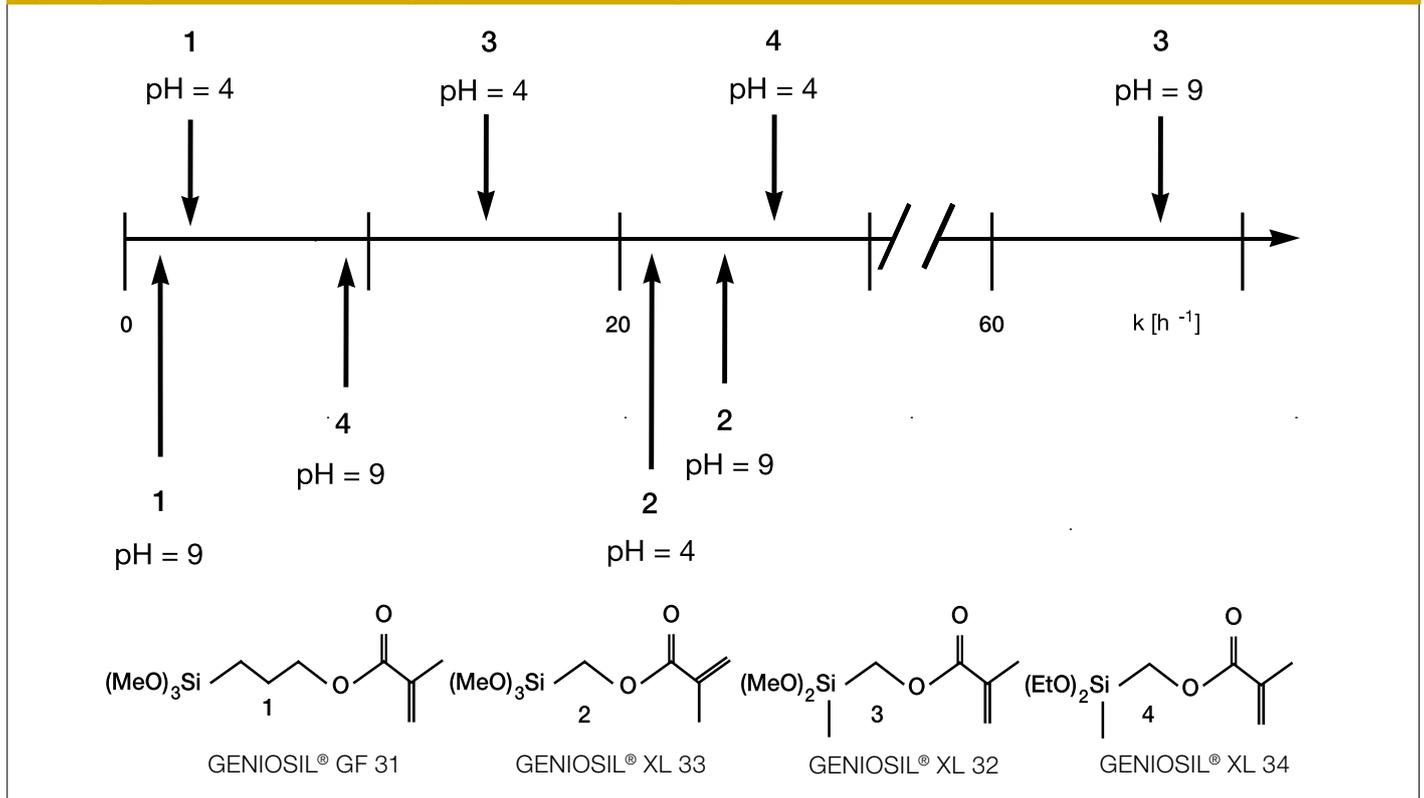
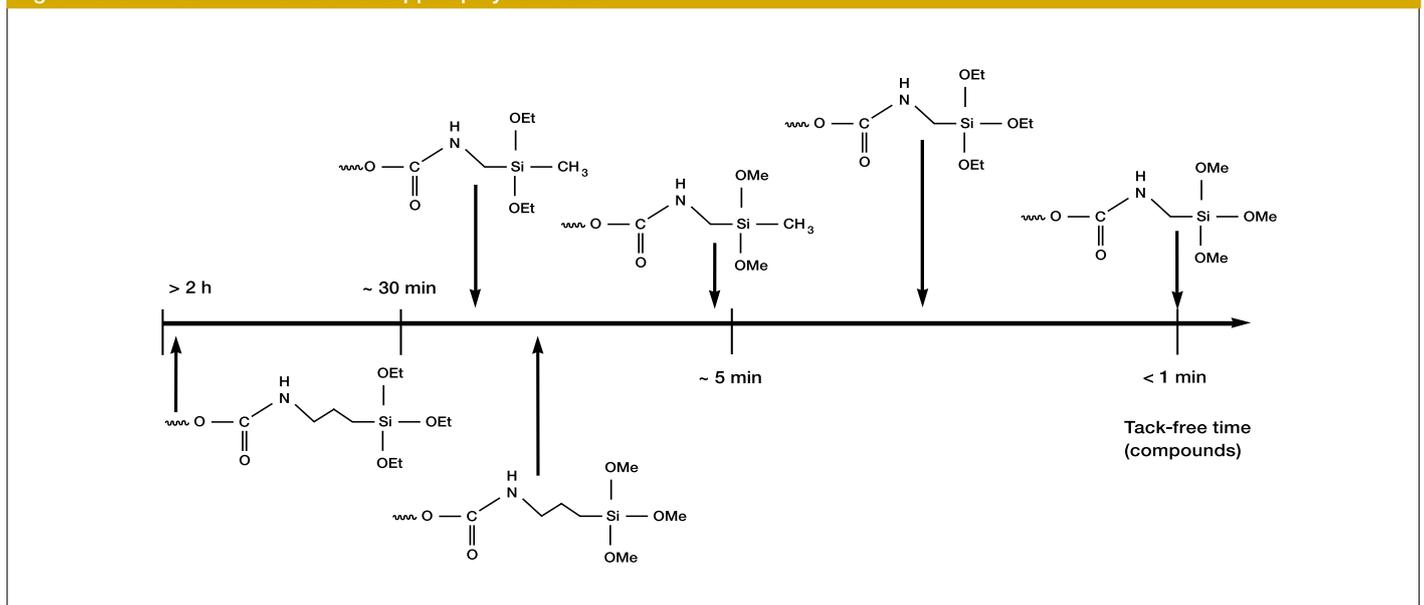


Fig. 4: Tack-free times of silane end-capped polyether diols



* GENIOSIL® is a trademark of Wacker Chemie AG

Again, a very broad range of reaction rates can be observed, reflecting in this case both the hydrolysis and the condensation reaction. In combination with various possibilities to catalyze the curing process, pot lives relevant to many applications in the coatings, adhesives or sealants field can be adjusted.

From the data obtained so far, three important conclusions indicating the behavior of organofunctional α -silanes compared to their γ -counterparts can be drawn:

- The hydrolysis and condensation rates of α -silanes vary over a much broader range compared to their γ -analogues and can be adjusted by choice of silane and/or catalyst system. Even compounds that are highly reactive but free of metal catalyst can be formulated.
- Difunctional α -silanes which allow reduction of the VOCs liberated during hydrolysis as well as adjustment of network densities still display a relatively high reactivity. In the case of γ -silanes, most difunctional versions prove to be too slow, which renders them unsuitable for a number of applications.
- Ethoxy α -silanes are also very reactive and can be used in applications where methanol liberation is prohibitive due to its toxicity, but high reactivity still remains desirable.

3. Organofunctional silane incorporation in resins for top-coat applications

In a first attempt to evaluate the potential of the GENIOSIL® α -silanes to improve the properties of coating systems, typical resins used in the automotive coating industry were

modified. This application was chosen because there is still a growing need for an improved property profile of the top-coats applied. The common systems currently used in this industry are often limited in their balance between chemical and scratch or mar resistance: if one of the properties is optimized the coatings do not show an acceptable level of performance in the second field and vice versa. The α -silanes are promising candidates for solving this problem because of their potential to provide highly crosslinked systems – with crosslink density being related to scratch or mar resistance – along with the benefit of the pronounced acid resistance of the formed siloxane bonds. Two different approaches were selected to obtain silyl-modified resins typically used for top-coat formulations. The first involved solvent-based copolymerization of methacryl-functional silanes with other unsaturated monomers. The second approach functionalizes polyester polyols with isocyanate-functional silanes in a polymer-analogous reaction as shown in **Figure 5**.

In both cases, resins which exclusively crosslink via the silyl groups were targeted to ensure that competing effects from a second crosslinking mechanism are eliminated as these would potentially result in misleading data.

Acrylic copolymers containing silyl groups with a solids content of about 60 % were obtained by radical copolymerization of 30 % silane, 20 % iBuMA, and 50 % styrene (molar ratio) in an aromatic solvent at 140 °C, using TBPEH as the radical initiator (**Table 1**).

Fig. 5: Silane modification by copolymerization and hydroxy-functionalization

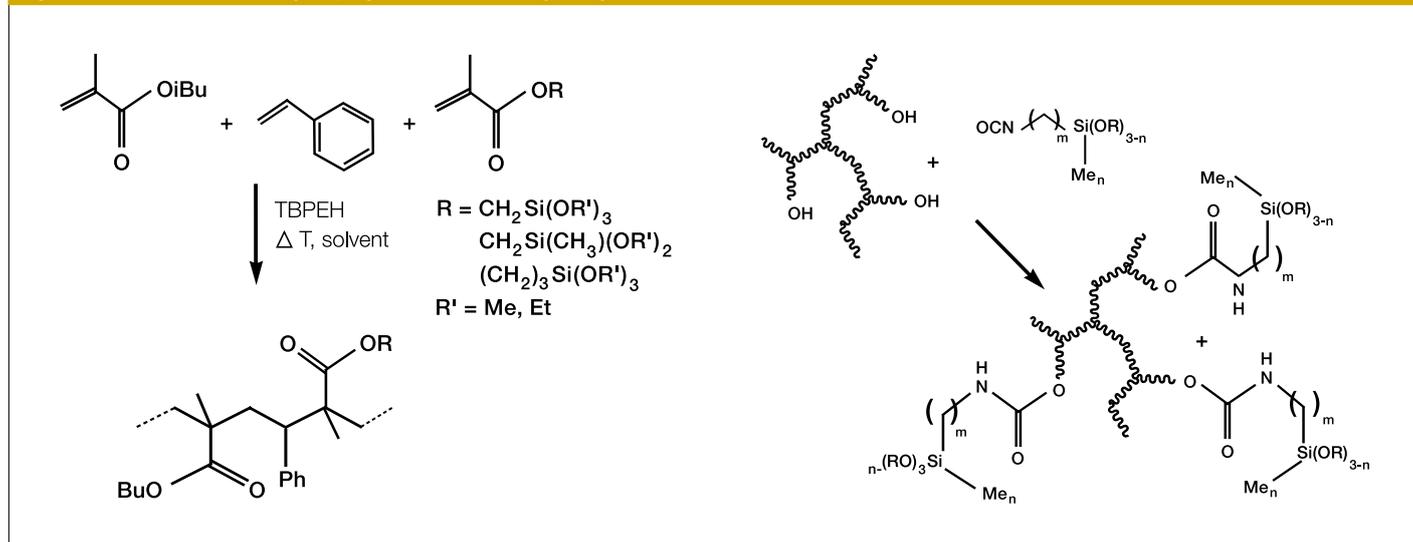


Table 1: Polymer properties of silyl-modified acrylics

Silane	Polymer	M _w	M _n	M _w /M _n	T _g [°C]
GENIOSIL® GF 31, 1	SPA-1	8633	1925	4.48	18
GENIOSIL® XL 33, 2	SPA-2	7562	2156	3.5	27
GENIOSIL® XL 32, 3	SPA-3	7223	1659	4.3	35
GENIOSIL® XL 36, 5	SPA-4	8985	2906	3.1	32
GENIOSIL® XL 34, 4	SPA-5	6481	1600	4.0	32
Reference, no silane ^{a)}	PA-1	4200	2200	1.9	10

a) Composition: 24 % EHMA, 10 % iBuMA, 20 % styrene, 42 % HPMA, 4 % AA (molar ratio).

Residual monomer contents of < 1% were achieved in all cases. The data shown in the table above clearly shows that incorporating the highly reactive α -methacryl-functional silanes **2 - 5** has no negative influence on the polymerization process. The lower T_g of the polymer obtained when copolymerizing the parent silane **1** presumably reflects the higher flexibility of the propylene spacer compared to the methylene group in **2 - 5**. Compared to a standard hydroxy-functional styrene-acrylic binder, somewhat higher molecular weights and broader molecular weight distributions are observed. This is presumably the result of traces of water leading to selective siloxane bond formation.

Silyl-modified polyester resins have been obtained by the reaction of polyester polyols with 3-isocyanatopropyltrimethoxysilane (commercially available under the tradename GENIOSIL® GF 40) **6** and isocyanatomethyltrimethoxysilane **7**, respectively. Three different polyols were used, one highly branched low molecular weight polyester polyol with a very high hydroxy number (**PE-1** available in undiluted form), a branched polyester (**PE-2**) and finally a linear version (**PE-3**), both with a moderate hydroxyl group content (available in an organic solvent). Functionalization was effected by addition of the polyester polyol to the isocyanate-functional silane at elevated temperature. Progress of the reaction can easily be monitored by the decrease in intensity of the specific absorption of the NCO group in the IR spectrum. The analytical

data of the polyester polyols as well as their silylated derivatives is given in **Table 2**. The functionalization is straightforward and proceeds quite smoothly. The reactions are complete within 3 hours at 80 °C. Almost no undesired cross-linking by reaction of the alkoxy groups of a functionalized polyester with a second polyol molecule, which would lead to a strong increase in viscosity, occurs.

4. Coatings from silane modified polymers

The silylated polyacrylates **SPA-1 – SPA-5** were applied to glass plates with a 100 μ m doctor blade after addition of 0.5 wt% of an amine-blocked para-toluene sulfonic acid (based on solids), and 0.01 wt% of a silicon-based flow and leveling agent. After curing for 30 minutes at 130 °C and storage for 72 hours (23 °C, 50 % rel. humidity), properties of the resultant films were investigated (**Table 3**). In addition, two reference coatings containing the polyacrylate **PA-1** were formulated for comparison.

As expected, the acid resistance of reference formulation **PA-1, 1K** which was cured using a melamine resin, was very low, whereas the hardness was comparable to the silane-crosslinked films. In the case of the reference PU coating **PA-1, 2K**, acid resistance was excellent, whereas pencil hardness was relatively low. The best overall property profile was obtained from **SPA-2** and **SPA-4** containing GENIOSIL® XL 33 and XL 34, respectively.

Table 2: Polymer properties of silyl-modified polyesters

Polyester polyols					Silylated polyester			
Name	OH number	Viscosity [mPa*s] ^{a)}	Solvent	Character	Name	Silane	Viscosity [mPa* s] ^{a)}	Residual NCO [%]
PE-1	330	600	none	branched 100 %	SPE-1A	6	1470	0.01
					SPE-1B	7	1300	0.009
PE-2	126	550	30 %	branched	SPE-2A	6	900	0.016
					SPE-2B	7	1200	0.008
PE-3	135	290	20 %	linear	SPE-3A	6	900	0.006
					SPE-3B	7	1100	0.002

a) Determined at a shear rate of 10 s⁻¹. All resins show Newtonian behavior (from 1 to 100 s⁻¹).

Table 3: Properties of silane-modified acrylic coatings

Resin	Gloss, 20° [GU] ^{a)}	MEK rubs ^{a)}	H ₂ SO ₄ ^{b)}	Crosshatch ^{a)}	Pencil hardness ^{a)}
SPA-1	178	> 100	> 504	4B	H/2H
SPA-2	162	> 100	> 504	4B	2H/3H
SPA-3	175	> 100	> 504	5B	H/2H
SPA-4	175	> 100	> 504	4B	2H/3H
SPA-5	166	> 100	> 504	5B	H/2H
PA-1, 1K ^{c)}	179	> 100	< 24	5B	2/3H
PA-1, 2K ^{c)}	175	> 100	> 504	5B	F/H

a) According to DIN EN ISO 2813, ASTM D 5402, ASTM D 3359, and DIN EN 13523-4.

b) A droplet of 30 % sulfuric acid was put onto the cured coating, covered with a cup and stored at 23 °C at 50 % relative humidity.

Every 24 hours it was checked whether a visible change could be observed after removal of the acid droplet, rinsing with water and drying.

c) PA-1, 1K was formulated from acrylic polymer PA-1 using a methylated melamine resin (60/40 based on solids).

In the case of PA-1, 2K, a standard HDI trimer was used as a curing agent.

In addition to the above tests, gloss retention of the coatings was determined, using a crockmeter-like scratching device. The retained gloss after 100 scratch cycles under a 500 g load was determined (Figure 6).

The reference system **PA-1, 2K** showed the typically low scratch resistance of a PU coating compared to a top-coat cured by a melamine resin as in the case of **PA-1, 1K**. In addition, it becomes obvious that the α -silanes can lead to a strong increase in scratch resistance when incorporated into an acrylic polymer both compared to the standard silane **1** and the melamine-cured reference system **PA-1, 1K**, while still offering excellent acid resistance. Surprisingly, the ethoxy derivatives give the best scratch resistance, a result which is still under evaluation.

In order to obtain applicable coating systems from the silylated polyesters **SPE 1A – 3B** the following formulations were prepared (Table 4).

These formulations were reduced to a solids content of 60 % by addition of MPA and applied to glass and steel plates again using a 100 μ m doctor blade. Curing was effected at room temperature. No heating was necessary.

Tack-free times of about 1 hour were observed (essentially resembling the time required for the solvent to evaporate). After 72 hours storage at ambient temperature, analysis of the coating properties as in the case of the silylated acrylates was performed (Table 5, Figure 7).

Table 4: Test formulations

Compound	pbw
Silylated polyester	100
N-Trimethoxysilylmethyl-O-methyl carbamate (water scavenger)	1
Butyl phosphate (10% in methoxy propyl acetate, MPA)	5
Silicon-based leveling agent	0.1

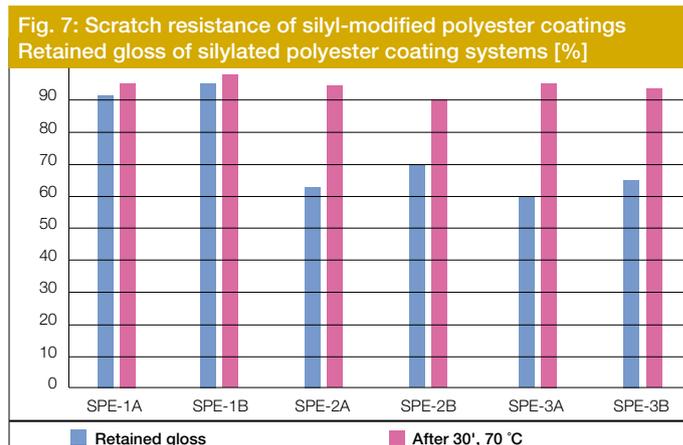
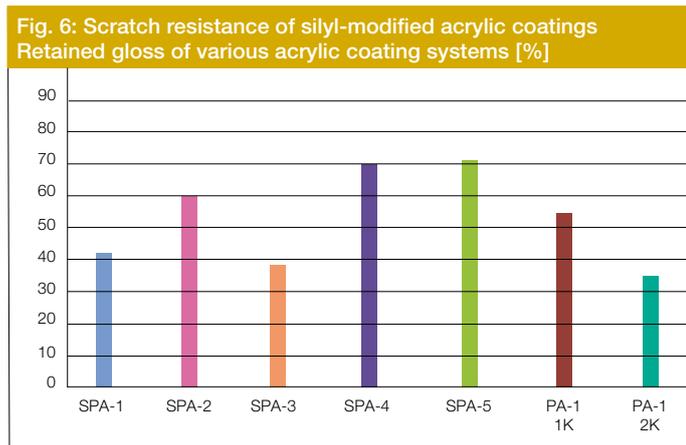


Table 5: Properties of silyl-modified polyester coatings

Resin	Gloss, 20° [GU] ^{a)}	MEK rubs ^{a)}	H ₂ SO ₄ ^{b)}	Crosshatch ^{a)} on glass	Pencil hardness ^{a)}
SPE-1A	165	> 100	> 504	5B	7H/8H
SPE-1B	164	> 100	> 504	5B	7H/8H
SPE-2A	168	> 100	> 504	5B	4H/5H
SPE-2B	170	> 100	> 504	5B	5H/6H
SPE-3A	171	> 100	> 504	5B	H/2H
SPE-3B	172	> 100	> 504	5B	2H/3H

a) According to DIN EN ISO 2813, ASTM D 5402, ASTM D 3359, and DIN EN 13523-4.

b) A droplet of 30 % sulfuric acid was put onto the cured coating, covered with a cup and stored at 23 °C at 50 % relative humidity.

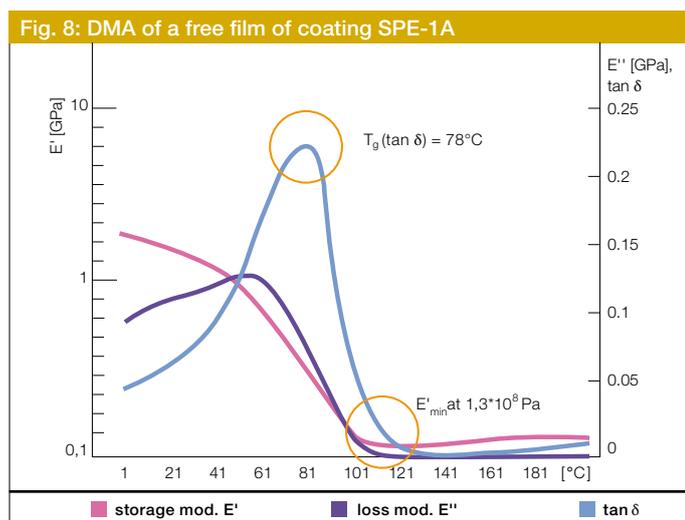
Every 24 hours it was checked whether a visible change could be observed after removal of the acid droplet, rinsing with water and drying.

Excellent chemical resistance as well as pencil hardness was observed for all coating formulations. In addition, also the scratch resistance in the crockmeter test turned out to be very good. In general, the mechanical data reflects the crosslinking density as implied by the varying functionalities of the polyester polyols.

The extraordinarily high scratch resistance observed for the silylated polyester coatings **SPE-1A** and **SPE-1B** may result from a combination of a very high crosslinking density and a moderate T_g as found in a DMA of a free film of **SPE-1A** (**Figure 8**): a storage modulus E'_{min} of $1.3 \cdot 10^8$ Pa (at 115 °C) along with a T_g of 78 °C (from $\tan \delta$) were found (typically, E'_{min} values of 2.5 - $3.5 \cdot 10^7$ Pa are obtained with isocyanate or melamine crosslinked polyacrylate coatings).

This corresponds to a crosslink density M_c of about 78 (!) g/mol [5]. In addition, all systems investigated show very good recovery behavior.

Surprisingly, differences between binders modified with α - and γ -isocyanate silanes, respectively, were not as pronounced as in the case of the silylated polyacrylates. The reasons for this unexpected observation are still under investigation.



5. Conclusion

Organofunctional α -silanes of the GENIOSIL® series have been presented with organic functionality of known behavior that display a unique hydrolysis and condensation reactivity profile on the silane moiety. This combination opens up many opportunities for coating systems and potentially offers improved performance such as scratch resistance, reduced curing times and/or temperature (due to higher reaction rates), low VOC systems as well as non-toxic cross-linking systems.

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