

Nathalie Havaux, Christophe Steinbrecher and Denis Heymans, Hexion Research Belgium SA, discuss the company's novel isocyanate-free 1&2K moisture-cure technology as a cost effective alternative to 2K polyurethanes

A cost-effective alternative to 2K polyurethanes

Acrylic- and epoxy-alkoxysiloxanes are increasingly used in moisture-curing isocyanate-free resins for marine and protective applications. These resins are valuable alternatives to 2K polyurethanes due to their broad range of performances and their ability to cope with recent environmental trends. Their market penetration, however, has been limited so far due to an unfavourable cost/performance ratio.

A new family of polymers based on the combination of vinyl (neo)ester and vinyl alkoxysilane monomers is presented in this paper. These polymers, with solid content between 70–100%, offer attractive properties by varying process parameters, monomers composition and alkoxysilane levels, as well as an attractive cost level.

This new, highly versatile, binder technology was tested in 1- and 2K moisture-cure coatings with standard catalysts. The tests demonstrate that high solids content, fast drying development and long shelf life can be combined in a cost-efficient and isocyanate-free solution. The performances of these vinyl silane copolymers enable the development of a new range of valuable alternatives to 2K polyurethanes and acrylic-alkoxysiloxanes for many applications, especially in protective coatings.

■ MOISTURE CURING ALKOXYSILANES

Today, silicone-containing coatings are specified for a wide range of steel constructions, including highly demanding applications, such as offshore platforms, storage tanks and pipes. They are particularly appreciated for their very high durability and have often replaced polyurethanes. Coatings based solely on polysiloxane resins, however, have limited market penetration. Instead, silicone coatings usually combine an inorganic polysiloxane with an organic resin¹. Most leading protective coatings suppliers offer silicone-containing coatings based on epoxy-polysiloxane and/or acrylic-polysiloxane chemistries. In both cases, an inorganic polysiloxane resin is reacted

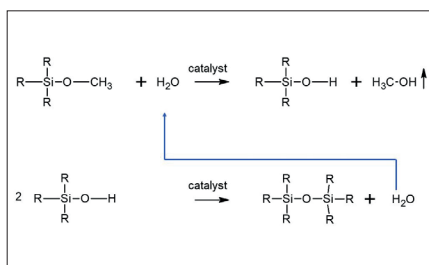


Figure 1. Moisture curing of alkoxysilane-based coatings

with the organic epoxy or acrylic resin to balance and optimise properties like shelf life, viscosity, durability, cohesive strength and adhesion. To achieve optimal performance, the typical level of a methyphenyl polysiloxane ranges from 37 to 77wt%¹, which brings the cost of these systems to excessively high levels.

In the case of acrylic-silane systems, curing happens only via the inorganic hydrolysis-condensation sequence of the silane groups². These systems are manufactured via radical copolymerisation of silane-functional acrylates and (meth)acrylate monomers, most commonly, gamma-methacryloxypropyl trimethoxysilane (MPTMS).

Once a silane functional coating is applied, the moisture curing process occurs in two steps. In the first step, the silane reacts with water to yield a silanol. In the second step, two silanol groups condensate to form a siloxane bridge, with the release of one molecule of water (**Figure 1**). Half of the water consumed in the first step is, thus, released in the second step, ensuring further curing deeper into the coating. Sometimes a mix of different catalysts is required to promote these hydrolysis-condensation reactions.

In theory, alkoxysilane-based acrylics could be formulated as single-component (1K) systems. The coatings should not begin to cure until they are applied to a surface and exposed to air and moisture. However, pigments and additives used in paint formulations usually contain some moisture, which can initiate premature curing in the can³. Numerous solutions have been proposed to solve this issue,

some with success. Certain solutions are based on the use of moisture scavengers⁴ while other use mixtures of reactive polysiloxanes and silane-free acrylic resins⁵.

Despite their high apparent potential, 1K moisture-cure alkoxysilane-acrylics have so far only achieved a limited market penetration. The high cost of MPTMS monomer and the polysiloxane resins is probably partly responsible for this.

■ NEOCARBOXYLIC ACID-BASED MONOMERS

For more than 50 years, neocid-based monomers find most of their applications in the world of coatings, where they are well known for upgrading the performance and quality of vinyl, acrylic, polyester and other resins. The most common monomers used in these applications, based on C10 neocids, are glycidyl neodecanoate and vinyl neodecanoate, with three to six methyl groups per molecule.

The chemical structure of these vinyl and glycidyl monomers, with a high number of methyl groups, contributes to several attractive properties. Vinyl neodecanoate homopolymer has a critical surface tension as low as 24dyn/cm⁶ and provides high contact angles to derived coatings. Moreover, the tertiary structure of the original acid ensures excellent chemical stability and the absence of aromatic structures explains excellent UV resistance. Vinyl neodecanoate and neononanoate are well known by resin and paint producers under their tradename VeoVa™ 10 and 9 monomers. The homopolymer Tg's of these monomers are -3 and +70°C, respectively. In the frame of the present work, an important difference between vinyl and (meth)acrylate is the reactivity of the respective double bonds in radical polymerisation processes, as will be discussed below.

■ VINYL SILANES

Vinyl trimethoxysilane (VTMOS) and the related vinyl triethoxysilane (VTES) are bi-functional compounds, featuring both

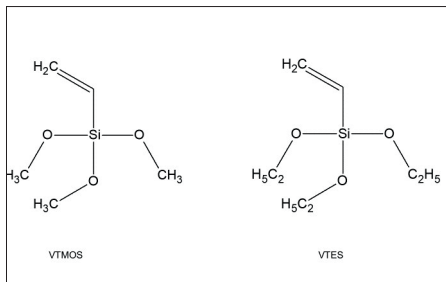


Figure 2. Common vinyl silane monomers

a vinyl group and highly reactive alkoxy groups in the α -position (**Figure 2**). VTMS is very well known by coating formulators as an efficient and affordable water scavenger. The vinyl group, on the other hand, has relatively low reactivity and needs highly activated radicals to be efficiently incorporated into polymer backbones by radical polymerisation. Attempts to build VTMS into (meth)acrylate polymers have therefore, faced severe issues of final monomer conversion⁷.

COPOLYMERISATION OF VINYL SILANES AND VINYL ESTER MONOMERS

The present work attempts to combine vinyl silanes and hydrophobic vinyl esters into affordable and high-performance polymers for 1K, moisture curing protective coatings. The reactivity ratios between these monomers were estimated using an e and Q scheme, as proposed by Alfrey and Price⁹. Results show that calculated r_1 and r_2 are actually very close to 1. For example, for the couple $M_1/M_2 = \text{VeOVA}10/\text{VTMS}$, $r_1 = 0.77$ and $r_2 = 1.27$. This means that vinyl silanes should distribute evenly in vinyl esters copolymer backbones, which is ideal for a crosslinker to provide high performance.

EXPERIMENTAL

The resins presented below combine vinyl alkoxy silane monomers with vinyl

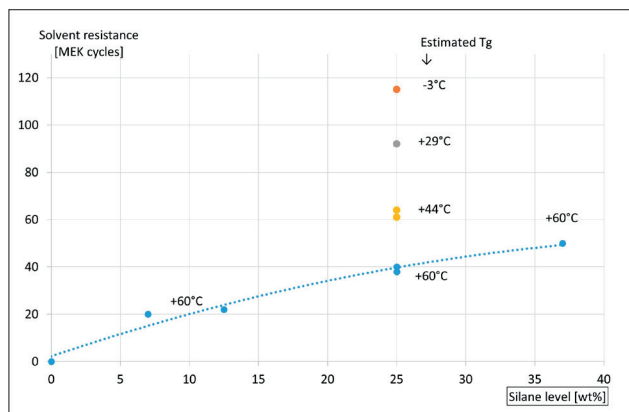


Figure 3. Effect of the level of silane and resin Tg on solvent resistance of clearcoats

Composition	Weight phm (per hundred monomers)	Purpose
Vinyl silane	0-35	Crosslinking
Methacrylic silane	0-15	Higher curing rate
VeOVA 9	0-100	High Tg (70°C) vinyl ester
VeOVA 10	0-100	Low Tg (-3°C) vinyl ester
Organic peroxide	2-6	Molecular weight control
Butyl acetate	0-30	Dilution, viscosity control
Process	Variable	Purpose
Temperature	80-140°C	Molecular weight control
Reaction time	2-6hr	Ease of process

Table 1. Resin variables evaluated

neodecanoate (VeOVA 10 monomer) and vinyl neononanoate (VeOVA 9 monomer). Their detailed preparation procedure has been described in a recent patent application⁹. Monomers were chosen in order to combine the unique properties of neoacid derivatives, such as hydrophobicity and durability, with the moisture-curing mechanism of silanes. In the first part of this work, resins were optimised for their performance in clear and pigmented topcoats. In a second step, selected vinyl silane resins for clear and pigmented protective topcoats were benchmarked against commercial systems: 2K polyurethanes and 1K acrylic-polysiloxanes.

Resin optimisation

The variables were evaluated and the typical properties of resins are displayed in **Table 1**. In particular, the glass transition temperatures of the polymers were manipulated by varying the ratios between vinyl esters. The molecular weight of the polymers was varied by modifying the process conditions. The resulting vinyl silane resins were then formulated into 1K moisture-curable clear coats.

The various resins were mixed with catalysts and diluted with butyl acetate to the application viscosity (100 mPas). Films were then applied at 100µm wet with a barcoater and allowed to dry at 23°C and

50% relative humidity. The glass transition temperature (Tg) of the resins and the level and type of silane monomer were varied with the aim of optimising cure speed, solvent resistance and coating flexibility. **Figure 3** shows solvent resistance (MEK double rubs) of a series of clearcoats as a function of the level of silane after seven days of drying at room temperature. Additional clearcoats with 25wt% silane and Tg's ranging from +60°C to -3°C were also included in this evaluation. As expected, solvent resistance increases with the level of crosslinking monomers. However, the increase in solvent resistance with the decrease of the Tg may be somewhat surprising. This is possibly due to a limitation of the crosslinking density because of the reduced mobility of polymers with higher Tg.

Silane groups attached to polymers with lower Tg, however, may have more opportunity to crosslink and thus, to improve solvent resistance. This hypothesis is supported by the fact that the abrasion resistance of the clearcoats was also found to be better for resins with lower Tg. Further testing of both solvent and abrasion resistance of coatings cured at elevated temperatures supported this hypothesis.

Benchmarking exercise

Another series of resins was formulated into clear and pigmented topcoats (**Table**

	Methoxy Hydrophobic	Ethoxy Hydrophobic
Composition	[wt %]	[wt %]
Silane monomer	20	20
VeOVA 10	28	28
VeOVA 9	52	52
Properties		
Calculated Tg [°C]*	35	35
Solids content [wt %]	80.3	80.1
Mw (weight average)	16,700	21,700
Viscosity [Pas]	15.5	12.4

Table 2. Properties of the liquid resins used for benchmarking purpose. *Tg calculated with Fox equation considering only vinyl ester monomers

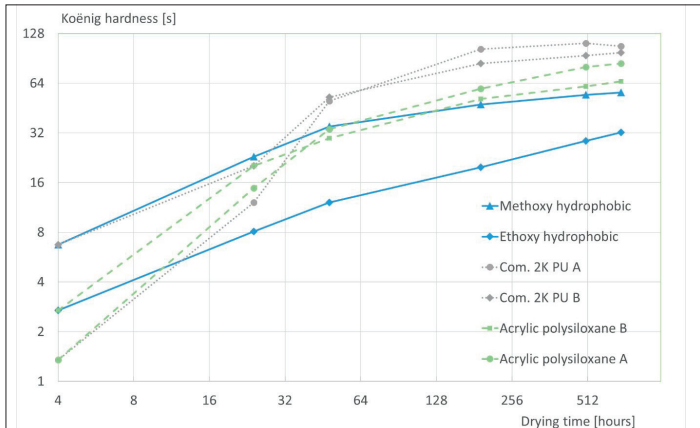


Figure 4. Hardness evolution of pigmented topcoats

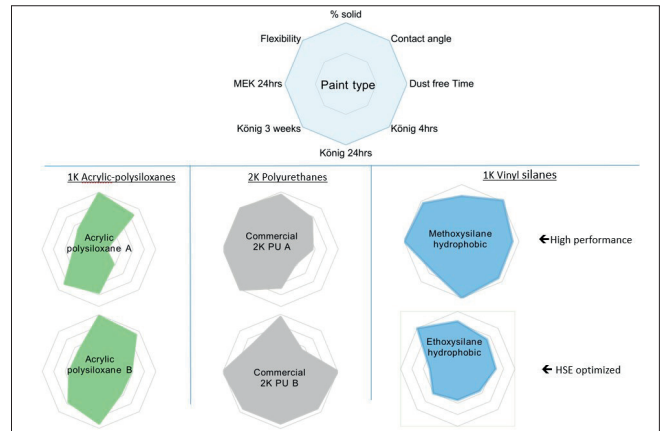


Figure 5. Properties of the vinyl silane pigmented topcoats compared with commercial benchmarks

2). A first resin was made using exclusively hydrophobic, branched vinyl esters (Veova 9 and 10 monomers) and methoxy silane monomers. In the second, resin ethoxy silanes replaced the methoxy silanes for HSE reasons. The performance of the corresponding coatings was compared with 2K polyurethanes and 1K acrylic-polysiloxane coatings (Table 3).

Clearcoat performance

Table 3 shows that these vinyl silane systems have very short dust-free time and fast early hardness development when compared to the 2K PU system. These are critical properties for professional painters as they enable a higher productivity. This is most probably due to the high molecular weight of the resins combined with a T_g above room temperature.

During the first four hours of drying, crosslinking of the methoxy-based vinyl silanes is also fast enough to ensure rapid hardness development and solvent resistance. The ethoxy silane system, on the other hand, cures slower as expected, yet also develops good performance over time.

PIGMENTED TOPCOAT PERFORMANCE

Figure 4 shows the development of König hardness of the vinyl silane resins (solid lines) compared to the commercial 2K PUs (dotted lines) and acrylic-polysiloxanes (dashed lines) benchmarks. As expected, both methoxy silane-based topcoats show excellent hardness development during the first hours of drying.

After three weeks, all polysiloxane systems exhibit lower hardness than the polyurethanes. Consequently, the softer vinyl silane systems exhibit better flexibility than the commercial acrylic-polysiloxanes (Table 3).

Figure 5, which shows the balance of properties of the various systems on radar charts, illustrates the versatility of this new technology very well. As can be seen, a significantly better balance of properties than the commercial acrylic-polysiloxane paints is obtained.

CONCLUSIONS

- This new approach based on the moisture-curing of vinyl silane

binders proved to deliver true 1K high performing protective coatings combining two major advantages versus 2K PU systems: end users do not need to mix components shortly before application; and the very long pot life saves the end users from the disposal of the unused formulated coating.

- Vinyl silane binders offer a true isocyanate-free solution combining better balance of properties compared to commercially available 1K acrylic-polysiloxanes, together with a reduced cost.
- The high versatility of this technology allows the development of high solids coatings with very fast early hardness development combined with good flexibility, excellent solvent resistance and final hardness.

Properties:	Viscosity as applied [mPas]	Solids content applied [Wt %]	Water contact angle [°]	Dust-free time [min]	König hardness after			MEK resistance after		Conical mandral flexibility after 3 weeks [mm]	Gloss @ 60° [%]
					4hrs	24hrs	3 weeks	24 hrs	3 weeks		
Clearcoats:											
Methoxy silane hydrophobic	290	64.0	91.5	8	8	30	75	76	>200	Failed (>25 mm)	85
Ethoxy silane hydrophobic	280	63.3	84.3	9	1	8	49	59	>200	< 23 mm	86
Commercial 2K PU	260	65.4	77.4	39	0	12	121	>200	>200	< 5 mm	94
Pigmented topcoats :											
Methoxy silane hydrophobic	800	61.5	90.7	18	7	23	54	>200	>200	< 7 mm	26
Ethoxy silane hydrophobic	750	65.5	81.8	24	3	8	29	47	>200	< 5 mm	40
Commercial 2K PU A (Hexion formulation)	nd	78.4	82.8	29	1	12	112	>200	>200	< 5 mm	95
Commercial 2K PU B (Commercial paint)	1000	79.3	75.7	16	7	20	94	>200	>200	< 18 mm	69
Acrylic-polysiloxane B	1150	82.3	87.5	28	3	20	61	55	160	Failed (>25 mm)	83
Acrylic-polysiloxane A	1450	83.2	85.6	129	1	15	80	29	>200	Failed (>25 mm)	79

Table 3. Properties of the vinyl silane and benchmark coatings

References

1. Erik Graversen, Hempel, *International Paint and Coating Magazine*, October 2011, 4-17.
2. R lezzi, J Martin, J Tagert, P Selbodnick, J Wegand and E Lemieux, NRL review, featured research, 2013, 1, 88-98.
3. Chang *et al*, PPG Industries Inc, US 4043953.
4. S Nixon *et al*, AkzoNobel Coatings International BV, European Patent EP 1 292 650.
5. S Nixon *et al*, AkzoNobel Coatings International BV, European Patent EP 1 587,889.
6. D Basset, *Journal of Coatings Technology*, 2001, 73, 43-55.
7. D Paquet *et al*, Dupont de Nemours, WO 2003078486 A1.
8. T Alfrey, C C Price, *J Polym Sci*, Vol 2, No 1, 101 (1947).
9. Heymans D and Romanowska C, Hexion Research Belgium, EP 3363827 A1.

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