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ALL-ROUND GAINS FOR POLYURETHANES

Thiol-silane oligomer avoids limitations of amino silanes. By Nayeem Soad, Dean Kondos, Dmitry Chernyshov, Vikram Kumar and Martin Wusik, Momentive Performance Materials.

A new low-odour oligomeric glycolic mercapto silane additive for 2K PU systems eliminates disadvantages associated with amino silanes, such as yellowing on exposure and shortened pot life. Improvements could be obtained in pot life, surface hardness, metal substrate adhesion and corrosion resistance.

This paper describes Momentive Performance Materials' new oligomeric glycolic mercapto silane known as "CoatOSil T-Cure" silane (*Figure 1*). This oligomeric glycolic, mercapto silane has very low odour compared to standard thiol-silanes, can behave as a reactive additive within a coating formulation, and may be used in any coating chemistries where thiol groups can react. The focus of this work is, however, on 2K polyurethane coatings. The effect of the silane on these coatings was studied using four types of formulation as described below. Addition of the silane to the formulations produced coatings that developed faster surface hardness with improved adhesion and corrosion resistance. Colour and gloss retention were not affected when exposed to UVA and UVB weathering. The new silane also enhanced the pot life of a 2K PU formulation containing a high content (wt)% of a tin catalyst, without greatly affecting cure time.

AVOIDING THE LIMITATIONS OF AMINO SILANES

While other silane additives, for example amino silanes, have been used to improve adhesion of urethane coatings, they have several disadvantages in these coatings. First, amino silanes react quickly with isocyanates, which shortens the pot life of the coating formulation and may affect other coating properties (such as adhesion). Second, the addition of amine functionality into the coating formulation can lead to yellowing upon exposure to UV radiation, thus limiting its use in outdoor applications.
In addition to the benefits described above, this silane can be added to either the part A or part B of 2K polyurethane formulations, providing more formulation latitude compared to an amino silane, which typically can only be added to the Part A side.

TEST FORMULATIONS, PREPARATION AND APPLICATION

Four types of 2K polyurethane coating systems were evaluated:

- Basic model clear coat
- Formulated clear coat
- Pigmented system
- Commercial topcoat/primer system

In each case, these were evaluated on various metal panels that were prepared and spray-coated following the protocol described below.
An alkaline metal cleaning solution was used to clean the metal panels. The cleaning solution was stirred under slow agitation and heated to a temperature between 65 °C and 70 °C. Panels were then fully immersed in this solution for two to three minutes to remove any oil contaminants.

RESULTS AT A GLANCE

➞ A coating additive based on a new oligomeric glycolic mercapto silane structure has been developed. This is a non-HAPS silane with little to no odour, a viscosity of approximately 300 cP, and less than one percent releasable ethanol.

➞ This product eliminates a number of disadvantages associated with the use of amino silanes, such as yellowing on exposure and shortened pot life.

➞ Incorporation of this silane into a two-component polyurethane produced coatings with improved properties, such as longer pot life, higher surface hardness, improved metal substrate adhesion and corrosion resistance.

➞ The gloss and colour of the coatings was also retained very well in UV weathering studies.

➞ The product can also bring benefits in other coating chemistries where reactivity with thiols can occur, making it a versatile, multi-functional, coating additive.

These panels were then removed from the solution and immediately rinsed with deionised water. High-pressure air was used to dry the panels. As a quality check to determine panel cleanliness, a few panels were tested for water breaks (the contact angle of water is close to zero degrees). If the misted water did not bead on the panels, the panel set was dried and stored in a desiccator for testing; otherwise, the cleaning process was repeated.

The coatings were applied to these cleaned metal panels cut to dimensions of 5 x 10 cm. Spray application was conducted using an HVLP gravity fed siphon spray gun. Gauge pressure near the gun was approximately 25 lb/in^2 (170 kPa).

The spray application was a side-to-side sweep of the spray gun, maintaining a gun to target distance of some 20 to 25 cm at a traverse speed of around 800 inches/minute (20 m/min), indexing up and down the panels at approximately one inch (2.5 cm) per sweep. Wet film builds were measured to achieve an approximate equal dry film build for further testing.

DETAILS OF THE FOUR DIFFERENT TEST COATINGS

A basic clear coat formulation (*Table 1*) was used to study corrosion resistance and adhesion to multiple substrates as well as the pot life of the coating formulation. Throughout this document, product formulations are included as illustrative examples only. Momentive makes no representation or warranty of any kind with regard to any such formulations. Similarly, test results relate only to these specific formulations. Actual results may of course vary.

The silane was incorporated into the part A side of the clear coat formulation (1.45 wt% based on total formulation) in the presence of "Fomrez SUL-4" (DBTDL, dibutyl tin dilaurate) and triethylamine (0.01 wt% catalyst); the part B side contained the hardener (isocyanate solution). A model 2K polyurethane clear coat formulation (*Table 2*) with different levels of silane (0.9 wt% and 2.9 wt% based on total formulation) was developed. Coatings prepared using this model clear coat were used to study corrosion resistance, König hardness and dry time.

The silane was also incorporated into a pigmented coating formulation (at 0.55% based on total weight) with the DBTDL and triethylamine catalysts (0.06 wt% based on total weight). The corrosion resistance of the pigmented polyurethane coating containing silane was evaluated.

The new mercapto-silane was also added into a commercial urethane primer system (*Table 2*) to determine whether it would enhance the performance of a standard product. Panels were coated with both the primer as purchased and the primer with silane added.

After the primers were cured, a topcoat (*Table 1*, last column) was coated onto the primed substrates. After curing for approximately one week at ambient conditions, samples were placed in their respective testing matrices.

Figure 1: Structure of the new mercapto-silane.

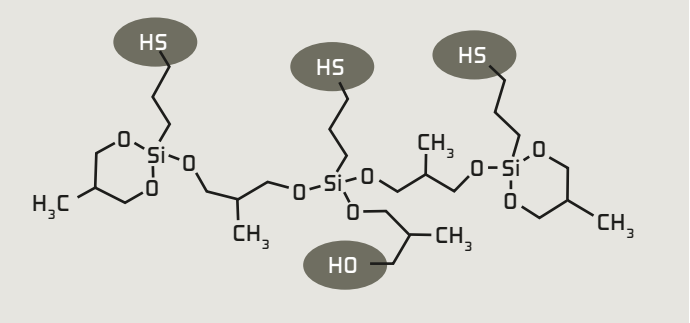


Figure 2: Corrosion resistance on galvanised metals, showing improvement due to silane addition.

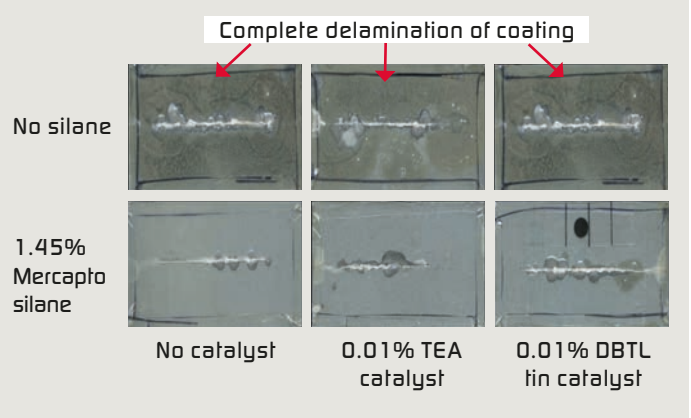
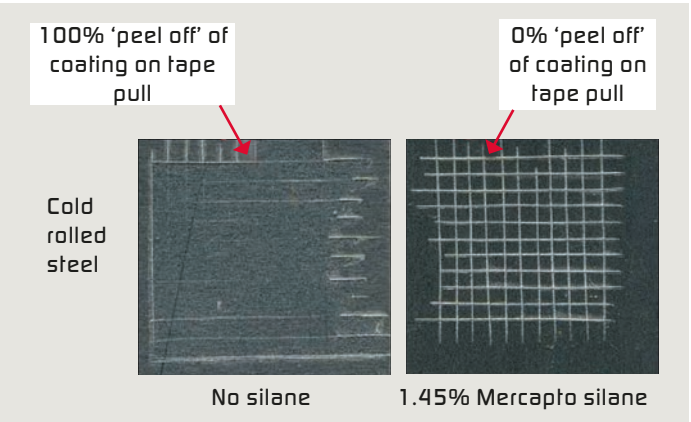


Figure 3: Adhesion test results; control vs. silane addition.



TESTING CARRIED OUT TO STANDARD PROTOCOLS

The following tests were conducted in order to evaluate the performance of the silane. Details regarding test protocols can be found in the following ASTM methods.

› König hardness (ASTM D4366–95)
› Dry time (ASTM D5895-03)
› QUV-B &QUV-A performance (ASTM G53-88)
› NSST- Corrosion resistance (ASTM D1654-92)
› Adhesion (ASTM D3359).

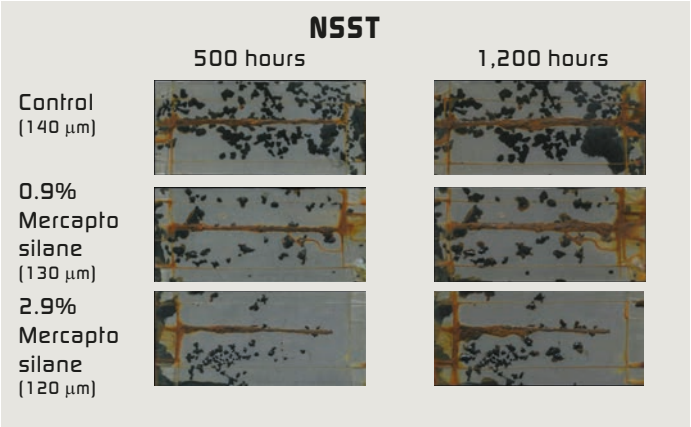
ADHESION AND CORROSION RESISTANCE MARKEDLY IMPROVED

Model clear coat formulations (*Table 1*) were spray coated onto different types of galvanised metal (skin pass hot-dip, non-skin pass hot-dip and electro-galvanised zinc) and the neutral salt spray corrosion resistance of the coatings was evaluated over 500 hours. The results in *Figure 2* indicate that the coatings without silane delaminated completely while those containing silane stayed intact even after 500 hours. The silane also significantly improved the corrosion resistance of the coating.

The corrosion performance was not limited to a specific type of metal substrate. Similar results were observed with skin pass hot-dip, non-skin pass hot-dip and electro-galvanised zinc. Adhesion to different types of metals, such as cold rolled steel, hot-dip galvanised and bare aluminium, was studied using the basic clear coat formulations (*Table 1*). The addition of the silane into the coating formulation significantly improved adhesion compared to the control (*Figure 3*).

Adhesion to cold rolled steel panels is illustrated in *Figure 3*. Similar performance was also observed on hot-dip galvanised (both skin pass and non-skin pass), electro galvanised zinc and bare aluminium substrates.

Figure 4: Corrosion resistance as a function of time and silane loading.



POT LIFE EXTENDED WHEN TIN CATALYST IS USED

Two part polyurethane coatings are known to have very short pot life under certain types of catalyst system (e.g., high levels of tin-based catalysts). Formulations (*Table 1*) using a high level of catalyst (0.25 wt% based on resin solid) and silane (1.45 wt% based on total coating weight) were prepared (*Table 1*) and the viscosity was monitored as a function of time.

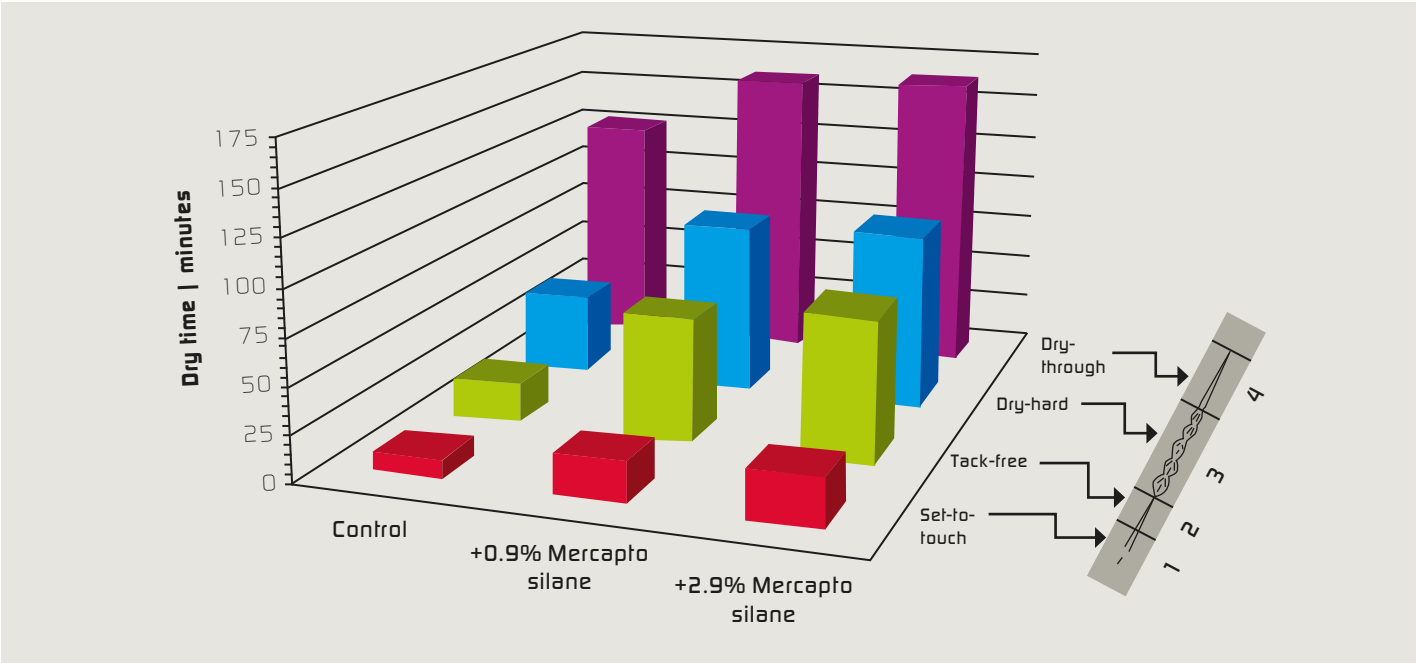
Table 3 shows the amount of time required for the initial viscosity to double under different catalyst system. Data from this table shows that the addition of the silane had little to no effect on pot life for both non-catalysed and amine catalysed coating systems.

However, in coatings catalysed with DBTDL tin catalyst, the addition of silane resulted in a dramatic increase in pot life compared to the same formulation without it. The control, tin catalyst only system, doubled in viscosity in less than 30 minutes, whereas the tin plus silane system doubled in viscosity after 95 minutes.

CORROSION RESISTANCE AND HARDNESS IMPROVED

Various levels of mercapto-silane were incorporated into the formulation listed in *Table 1* and coated onto cold rolled steel panels. The neutral salt spray corrosion resistance, dry time, König hardness and UV stability of the cured coatings were evaluated. Panels were tested for 1,200 hours in neutral salt spray (NSST) and corrosion resistance

Figure 5: Clear coat dry times as a function of silane in formulation.



performance was monitored as a function of time. Samples containing the silane had better corrosion resistance when compared to a control sample without (*Figure 4*).
Drying times were measured using a dry time recorder utilising brass weights (5 grams). The recorder was run for six hours and thickness of the films was ca. 45 µm. Cure speed of clear coats are shown in *Figure 5*. The addition of silane did not have a significant impact on dry time.
Figure 5 shows the dry-through time for the control was 127 minutes and 165 minutes for the formulation with the highest loading of silane (0.09 wt% on total formulation). Thus, the silane did prolong the cure time by approximately half an hour, but this is not significantly higher than the control and is well within the acceptable range for most applications. Panels were cured at room temperature, and surface hardness (*Figure 6*) was measured as a function of time. This data indicates coatings containing the silane developed hardness faster and had a higher hardness once the coatings were fully cured.

CORROSION RESISTANCE OF PIGMENTED COATINGS IMPROVED

Pigmented coating formulations with and without the silane (*Table 1*) were coated onto skin pass hot-dip galvanised metal panels and cured for one week at ambient conditions. The corrosion resistance of the cured panels was tested in neutral salt spray for 500 hours. Coatings without silane delaminated completely while the coatings using the silane did not show any delamination (*Figure 7*).
The silane can also enhance the performance of a commercial urethane primer. The primer (*Table 2*) with and without silane was coated onto cold rolled steel panels and cured for 36 hours at room temperature. The top coat (*Table 1*) was then coated onto the primed panels. The cured film thickness of the primer was ~ 4 mils (100 µm) and the film thickness of cured top coat was ~ 4-5 mils (100-125 µm). The panels coated with the top coat were post cured for ~10 days and the adhesion and corrosion resistance were tested. Test data are shown in *Figure 8*.

Figure 6: Coating hardness as function of time and wt% mercapto-silane.

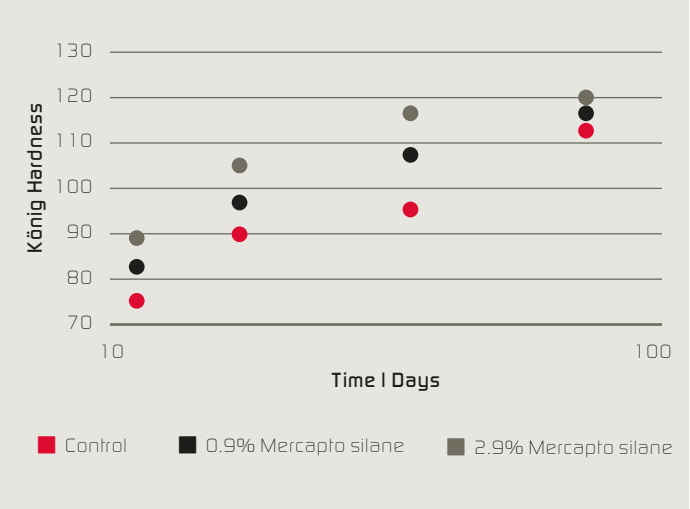
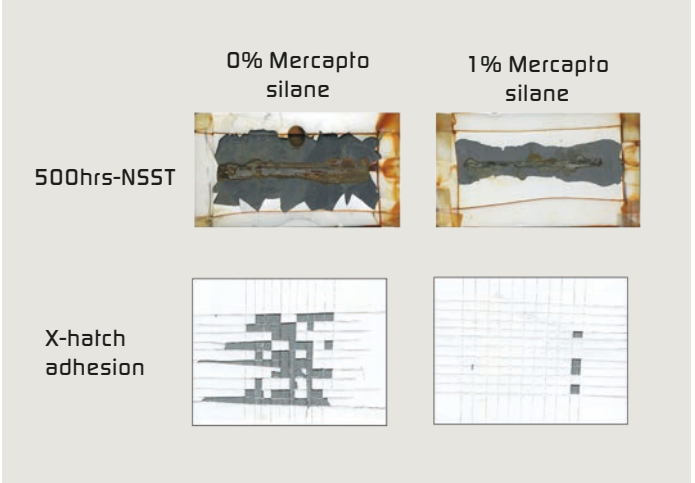


Table 1: Formulations for clear coats and pigmented system.

	Basic clear coat	Model 2K clear coat	Fully formulated system
PART A			
Commercial acrylic polyol	71.8		28.52
Acrylic polyol		46.37	
Fumed silica		0.20	
TiO_2 (pH ~ 6.5)			14.97
Talc (1.2 µm)			10.29
Kaolin (pH ~ 6.0)			6.55
Zinc phosphate			8.42
CoatOSil 7001 silicone copolymer		0.09	0.47
Tinuvin 328 UV absorber		1.14	
Tinuvin 292 light stabiliser		0.31	
DBTDL catalyst		0.09	
N-butyl acetate		17.56	16.83
Methyl ethyl ketone		8.11	
Xylene			7.48
PART B			
Isocyanate	28.2		
HDI trimer		18.22	6.48
N-butyl acetate		7.82	

Figure 7: Corrosion resistance of pigmented coatings with and without the silane.

Figure 8: Adhesion and corrosion resistance data of a commercial system with and without the silane.



"Very light odour."

3 questions to Dmitry Chernyshov

Mercapto silane interacts with the catalyst DBTL which is under environmental pressure and will be substituted e.g. by different metal complex catalyst. How is the interaction of this modern catalysts with the mercapto silane? *In general, tin is not an exception. Other transition metals such as Ti, Bi, Zn and the like will readily complex with –SH functionality. My suggestion will be to explore possibilities to work with tertiary amino technology. DBU or DABCO-type catalytic systems can be very efficient even at very low application levels (ppm).*

The addition of mercapto silane extends the drying time, probably in combination with DBTL. How could the impact of alternative DBTL catalyst be described to drying times? *As far as metal type catalytic systems are concerned I should expect the similar phenomenon, namely thiol-silane structures will slow down catalyst reactivity. If we are talking about thiol-urethanes or polyurethanes in general – the maximum output with drying time kinetics can be achieved with amino-type systems. For example, the same products as mentioned in the previous answer can be a good match.*

How do the results with regard to odour compare to conventional amino silanes? *"CoatOSil T-cure" silane is a very capable product and it has very light odour which is not irritating. In addition, it is an oligomer, which implies that the product has a relatively low volatility with respect to specific vapor pressure. On the contrary, conventional aminosilanes are highly volatile amines with very strong ammonia-type odor. Thus, as far as an odor perception is concerned - with the product there are very good results for coating formulators.*

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Incorporation of the silane into the primer system significantly improved adhesion compared to the control without silane. The corrosion resistance (500 hr neutral salt spray) of the coating formulation containing silane in the primer showed a significant improvement when compared to coating formulation without silane in the primer.

DIFFERENCES IN REACTIONS OF SILANES IDENTIFIED

To help explain the results described above and also to highlight the value of this new silane over other potential candidates (such as primary amino silanes), the silanes were added directly to an isocyanate (HDI trimer).
The addition of 1 wt% of primary amino silane into HDI trimer immediately resulted in a white precipitate. However, when 1 wt% of the new silane was added to HDI trimer no such precipitate formed.
The fast reaction of primary amino silanes with isocyanates can result in a shortened pot life for polyurethane coating formulations, which may affect other coating properties (e.g. adhesion). Second, the addition of amine functionality can lead to yellowing upon exposure to UV radiation, thus limiting their use in outdoor applications.
In addition, reaction kinetics were monitored using FTIR and it was found that the silane can react with isocyanate groups to form thiourethane groups.

WIDE RANGE OF BENEFITS FOR SEVERAL COATING TYPES

A new oligomeric glycolic mercapto silane additive has been developed. When added to 2K polyurethane coatings, this silane can enhance hardness, adhesion, corrosion resistance and the UV stability of the coating.

In addition to improving coating properties, the silane can also increase the pot life of a 2K polyurethane system that contains a tin catalyst. This product can be added to either the part A or part B side of a 2K polyurethane coating system.
In addition to urethane coatings, it may be considered for use in other coating systems (e.g. epoxy, acrylate etc.) where thiol reactivity is available.

Table 2: Modification of commercial primer with silane.

Part A	**wt%**	**wt%**
Commercial primer	89.58	88.77
1% mercapto-silane	0	0.9
Part B	**wt%**	**wt%**
Activator	10.42	10.33
Total	**100.0**	**100.0**

Table 3: Pot life of coating formulations with and without silane.

Pot life (minutes)	**0 wt% silane**	**1.45 wt% silane**
No catalyst	210	220
0.25% TEA	220	220
0.25% DBTDL	< 30	95