One Evolutionary Path of Organofunctional Silanes: AlkoxySilane Functional Silicones and their Applications

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For many decades now, organofunctional silanes have been used as surface treatments, adhesion promoters, dispersants or for cross linking in condensation cured systems. These monomeric materials are generically represented by $(R^1O)_3Si\text{-}R^2$. The R^1 alkoxy groups are often methyl but ethyl, propyl, and other alcohols are used and have the effects of slowing down the reaction and liberating less toxic alcohols.

The R^2 group is varied quite a bit more. Alkyl groups such as methyl or octyl are commonly used as surface treatments providing water repellency or particle dispersion. Water soluble groups such as polyalkyleneoxide provide sheeting or particle dispersion in aqueous systems.

Often R^2 is reactive with all of the reactive functionalities represented from amine to NCO. These dual reactive materials are used to bond both with a surface and with an organic resin, for example in an adhesive to provide improved adhesion. Also, these can be reacted first with a resin setting it up for a secondary cure when dried which gives improved properties such as tear strength, adhesion, impact resistance, etc.

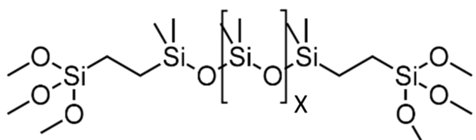
In nearly all cases, trialkoxy silanes first undergo an hydrolysis step forming organofunctional silanols which then undergo a condensation reaction with OH or similar groups on the surface, resin, or even another silane silanol group. In fact, difunctional dimethyl silanes are reacted with each other in this way to manufacture silicones.

Research in the 90's focused on increasingly more complex R^2 groups which quite often performed great in the lab but were not always cost-effective. In many cases, the improved properties could be achieved with high levels of standard organofunctional silanes at less cost.

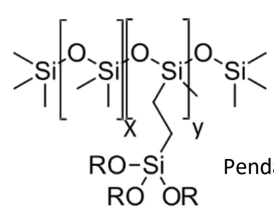
In this paper, we describe a simple direction that these silanes have evolved in over the years. The trialkoxy silane moieties are directly appended to silicone polymers forming a chemical chimera of both species.

Silane modified polymers.

This conceptually simple evolution of the trialkoxy silane monomer evolved from attaching silane monomers to silicone polymers. These Silmer® TMS branded polymers are available with linear di-functional or pendant multi-functional architectures.



Linear type



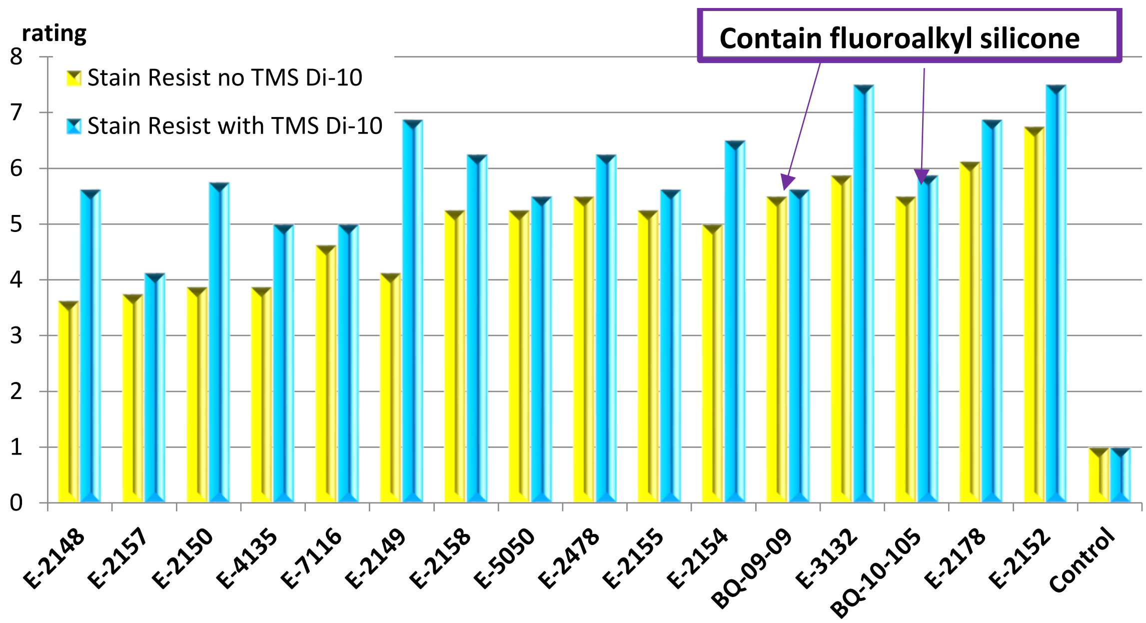
Pendant type

We have done a significant amount of application work with these polymers. In a typical set of data (Chart 1), a series of film forming emulsions[i] are applied to a white cotton fabric swatch, cured and subjected to stain testing with mustard, oil and vinegar dressing, and red wine. An average rating (1-10 best) is shown in the chart.

Two experimental emulsions, labeled with BQ series names, include fluorosilicone for added stain resistance. All of the film formers shown as yellow bars provide substantial protection relative to the untreated control.

In a second set of experiments, these film forming emulsions were upgraded with 7% of Silmer TMS Di-10 shown in the blue set of bars. The stain resistance is even further improved in this event. We have seen this effect of improved stain resistance from film formers further enhanced by Silmer TMS addition on aluminum, paper, leather and fiberglass surfaces.

Chart 1: Stain Resistance on Cotton

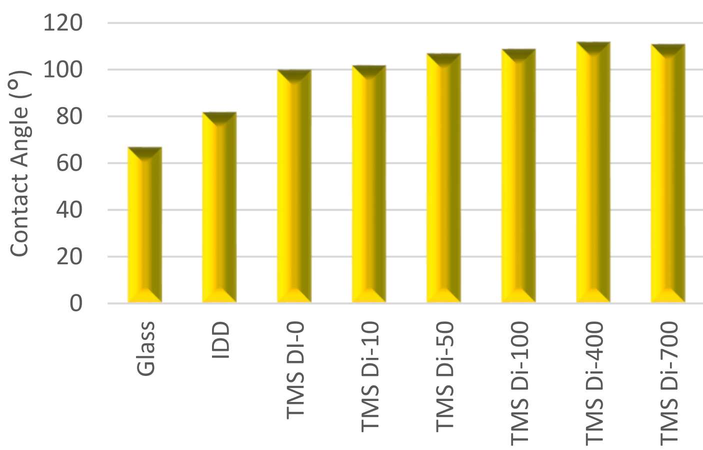


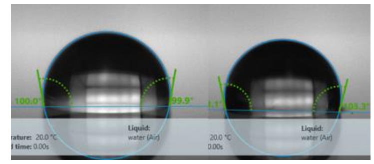
The improved stain repellency is believed to come from the hydrophobicity. We have not evaluated oleophobicity in most cases, but have seen enhanced stain protection from anchored silicones before.[ii]

Contact angles (Chart 2) of a series of linear Silmer TMS types on glass are shown against untreated glass and IDD treated glass. In general, the linear difunctional materials with highest values of x give the most impact on contact angle and stain repellency. We see similar trends on aluminum, fiberglass and paper.

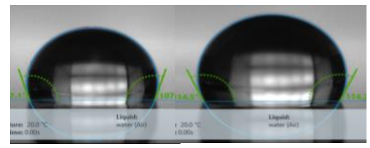
We have also shown these products to be effective in concrete treatments to minimize water pickup. Chart 3 shows a series of commercial and experimental Silmer TMS products evaluated for this purpose. The results are compared to no treatment and treatment with a basic film forming emulsion, Siltech E-2150. In this case, two pendant high MW materials show the best performance and all are superior to the controls. The experimental TMSF Di-H1 structure has fluoroalkyl groups on the backbone yet we can achieve the same performance without fluorine by using TMS C7.

Chart 2: contact angles on glass treated with linear Silmer TMS



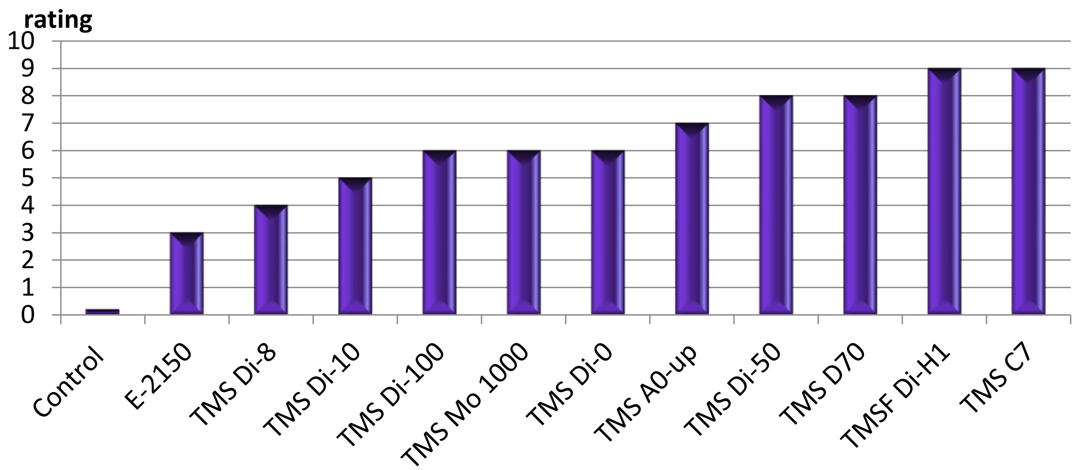


X=0, 100°; X=10, 103°



X=50, 107°; X-400, 115°

Chart 3: water pickup on Silmer TMS treated concrete tiles shown by rating (1-10 best)



Finally, in Chart 4 we show water uptake of treated concrete tiles which have been immersed. The Silmer TMS Di-50 and C-2053, a partially hydrolyzed version of TMS Di-10, show excellent performance. Pre-hydrolyzing these materials often shows an enhancement of properties.

Adhesion Promotion:

Regarding adhesion promotion, the accepted paradigm predicts that the polymeric silane containing materials would not be as effective at adhesion promotion as a monomeric trialkoxysilane. However, we find that using these polymers with monomeric silanes can show a synergistic improvement in adhesion. In this use lower MW TMS types such as Silmer TMS di-10 are more effective.

In Table 1, we evaluate two commercial silicone sealants with and without Silmer TMS and other promoters. One of two different catalysts are used. These blends are added at 2% loading and adhesion to PVC is reported as a rating 1-10 best. We find that we need an aminotrialkoxy silane or an aminosilicone (Silamine® D2 EDA or Silmer NH Di-8) with the Silmer TMS Di-10 additive to see substantial adhesion promotion. The very nucleophilic and basic primary amine seems critical to improving adhesion in these somewhat unique conditions.

Chart 4: water pickup on treated concrete tiles

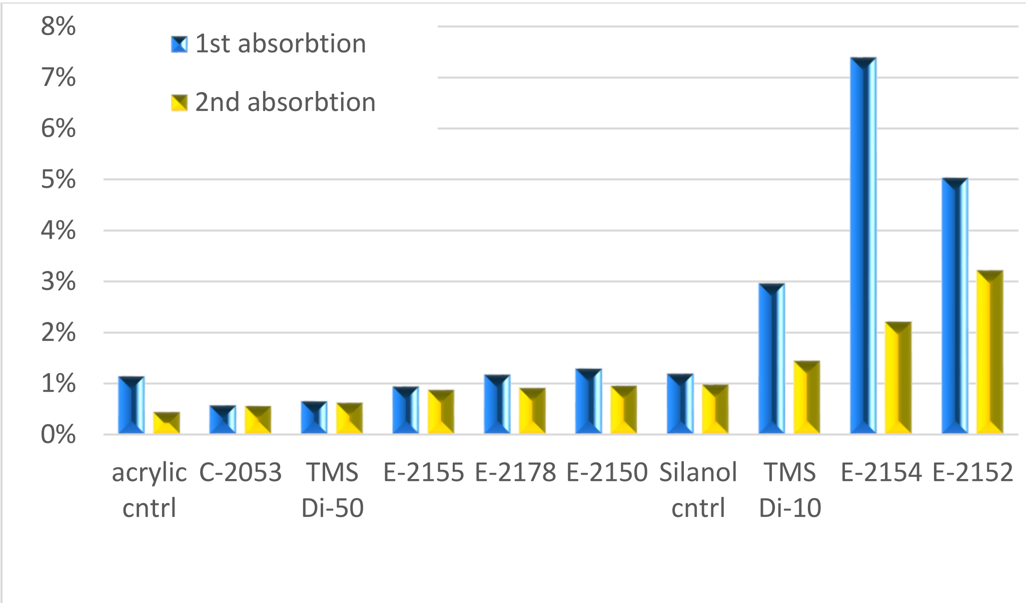


Table 1: various reactive silicones post added to commercial silicone sealants

Sealant	Additive A (1%)	Additive B (1%)	Catalyst	Rating 10 (best)
Commercial Sealant A			NaCure 4000	0
Commercial Sealant B			DBTDL	0
Commercial Sealant A	TMS Di-10		NaCure 4000	1
Commercial Sealant A	C-2053		NaCure 4000	1
Commercial Sealant A	TMS Di-8		NaCure 4000	2
Commercial Sealant A	NCO Di-10		NaCure 4000	2
Commercial Sealant A	NCO Di-10		DBTDL	2
Commercial Sealant A	TMS Di-0		NaCure 4000	3
Commercial Sealant B	TMS Di-10	Eugenol	DBTDL	3
Commercial Sealant A	Silmer NH Di-8		DBTDL	3
Commercial Sealant A	Silmer NH Di-8		DBTDL	3
Commercial Sealant A	Silmer NH Di-8		NaCure 4000	4
Commercial Sealant B	TMS Di-0	Silamine D2 EDA	NaCure 4000	5
Commercial Sealant A	Silamine D2 EDA		NaCure 4000	5
Commercial Sealant A	Silamine D2 EDA		DBTDL	6
Commercial Sealant A	TMD Di-10		DBTDL	7
Commercial Sealant A	TMS Di-0		DBTDL	7
Commercial Sealant B	TMS Di-10	Silamine D2 EDA	DBTDL	7.5
Commercial Sealant A	C-2053		DBTDL	8

Table 2: adhesion of silicone sealant enhanced with Silmer TMS Di-10 and aminopropyl silanes blends.

<table>
<tr><th>Additive A</th><th>Additive B</th><th>Ratio A:B</th><th>Rating 1-10 best</th></tr>
<tr><td rowspan="7">TMS type X=10</td><td rowspan="3">aminopropyltrimethoxysilane (no cat)</td><td>2:1</td><td>10</td></tr>
<tr><td>1:1</td><td>7</td></tr>
<tr><td>1:2</td><td>7</td></tr>
<tr><td>aminopropyltriethoxysilane (K-Kat 675)</td><td>1:1</td><td>9</td></tr>
<tr><td>aminopropyltriethoxysilane (K-Kat 651)</td><td>1:1</td><td>10</td></tr>
<tr><td>aminopropyltriethoxysilane (K-Kat 678)</td><td>1:1</td><td>10</td></tr>
<tr><td>aminopropyltriethoxysilane (K-Kat 670)</td><td>1:1</td><td>10</td></tr>
</table>

Table 2 shows adhesion promotion in a commercial silicone sealant. The Silmer TMS Di-10 polymer is blended with 3-aminopropyltrimethoxysilane in 2:1, 1:1 and 1:2 ratios or blended with the triethoxy analogue (1:1). The methoxy silane did not need catalysis, but the ethoxy version was catalyzed with several different catalysts. These blends are added to a commercial condensation cured silicone sealant at 5% loading and adhesion to PVC is reported as a rating 1-10 best. The improved performance with higher blend ratios of Silmer TMS Di-10 over the silane implies the polymer is improving adhesion.

Resin Modification:

Modifying resins to enhance performance is well known with silane monomers. This application also works with the Silmer TMS product. We have reported the effect of these materials on resins elsewhere.[iii] In that work, we showed Silmer TMS materials interacted with OH groups on a UV cured resin improving tear strength flexibility and hardness. In the interest of space, we will not further elaborate on that application herein.

Conclusions:

Traditional trialkoxy silanes are highly effective and useful products. What we have shown is that the silicone bound trialkoxy silanes are useful with reactive silicone polymers, enhancing the dried film properties of those polymers. Increased contact angle, stain resistance, and water resistance have all been demonstrated on paper, leather, concrete and aluminum surfaces.

Partially condensed silanes can be reacted and often provide enhanced properties.

Silmer TMS type silicone polymers with trialkoxy groups are very unique and offer enhancement of many properties when used alone or with other condensation reactive resins. They can be used alone or with traditional silanes to enhance adhesion promotion.

Further details and experiments are available upon request.

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[i] Steve Wilkowski et.al. **Reactive Siloxane Emulsions in Waterborne Coatings,** Proceeding of the Waterborne Symposium, **2018**, University of Southern Mississippi.
[ii]Bob Ruckle et.al. **Fluoro-Free Anti-Graffiti Properties from A Novel OrganoSilicone,** European Coatings Show **2017**, Vincentz press.
[iii] Bob Ruckle et.al. **Novel Silicone Materials Provide A Secondary Cure for Energy-Cured Silicone Acrylates** Radtech Europe **2019**.