Products for RTV-1 Silicone Sealants

Technical Information 1374

Evonik. Power to create.

Contents

1. Introduction

Silicone sealants have been an important and integral part of the sealants market for more than 40 years. To remain competitive in this large market in the future, producers of RTV-1 Silicone Sealants must develop innovative systems and solutions with an exceptionally wide range of products and services.

It is well known that AEROSIL® fumed silica can improve many properties of these silicone sealant compounds. Evonik Industries developed the AEROSIL® process more than 60 years ago and has been one of the leading companies in the development and production of fumed silica and fumed oxide.

AEROSIL® fumed silica can impart the required rheological and mechanical properties in RTV-1 Silicone Sealants. In addition to fumed silica, the use of AEROXIDE® fumed oxides and Dynasylan® silanes can provide unique properties in RTV-1 Silicone Sealants. Table 1 shows an overview of Evonik products developed for RTV-1 Silicone Sealants and their effects.

Table 1
Evonik products and their application options in RTV-1 Silicone Sealants

Effect	Product	Starting concentration (wt.%)
Reinforcement	AEROSIL® 150	5–15
Thickening	AEROSIL® 150	5–15
Improvement of storage stability	AEROSIL® R 972	5–15
Increase in transparency	AEROSIL® R 974 AEROSIL® R 106	5–15
High Temperature resistance	AEROXIDE® TiO_2 PF 2 AEROXIDE® TiO_2 P 25	0.5–1.5 0.5–3.0
Adhesion promotion	Dynasylan® product series	1.0–3.0
Mechanics (crosslinking)	Dynasylan® product series	2.0–5.0

In the following sections, the technical details of these Evonik products developed for RTV-1 Silicone Sealants will be discussed.

2. Technical fundamentals for the use of AEROSIL® and AEROXIDE® in RTV-1 Silicone Sealants

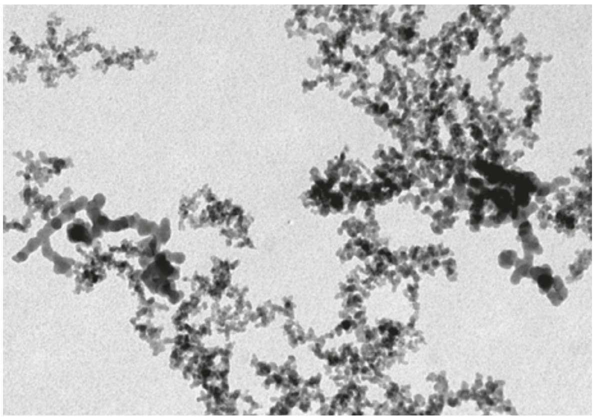


Figure 1
TEM micrograph of AEROSIL® 150

AEROSIL® fumed silica is an ultra-pure amorphous silicon dioxide with extremely small primary particles. These fine particles of high-purity white powder are produced by hydrolysis of chlorosilanes in an oxygen-hydrogen flame. The small primary particles give rise to very large specific surface areas ranging from 50 to 380 m^2/g.

Figure 1 exhibits TEM micrograph of AEROSIL® 150. The primary particles are not isolated but are linked together by covalent bonding to give stable aggregates, which can be a few hundred nanometers in size. The aggregates further form loose agglomerates with sizes of micrometers range, which can again disintegrate when dispersed in the application.

In addition to AEROSIL® fumed silica production, Evonik has applied the AEROSIL® process to other raw materials to produce fumed oxide (with the tradename AEROXIDE®) such as that of aluminum, titanium and others.

The development of special hydrophobic grades (surface modified with silane) of AEROSIL® and AEROXIDE® has enabled the production of advanced silicone sealants which helps shape the technologies of the future, for example, in vehicle construction and civil engineering. Table 2 and Table 3 list the physico-chemical properties of AEROSIL® and AEROXIDE® products.

Table 2
Typical physico-chemical data for AEROSIL®

		AEROSIL®							
		130	150	200	R 972	R 974	R 104	R 106	R 812 S
Surface modification		None, hydro-philic	None, hydro-philic	None, hydro-philic	DDS*	DDS*	D4*	D4*	HMDS*
BET surface area 1)	m^2/g	130 ± 25	150 ± 15	200 ± 25	110 ± 20	170 ± 20	150 ± 25	250 ± 30	220 ± 25
pH 2)		3.7–4.5	3.7–4.5	3.7–4.5	3.6-5.5	3.4–5.0	≥ 4.0	≥ 3.7	5.5– 9.0
Tamped density 3) (approximate value)	g/l	50	50	50	50	50	50	50	60
Compacted material with higher tapped density available on request?		Yes	Yes	Yes	Yes	Yes	Yes	No	No
Loss on drying 4) (2 h at 105 °C)	%	≤ 1.5	≤ 1.5	≤ 1.5	≤ 0.5	≤ 0.5	–	–	≤ 0.5
C content		-	-	-	0.6 - 1.2	0.9 - 1.5	1.4 - 2.0	1.5–3.0	3.0–4.0
SiO_2 5)	%	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8
Al_2O_3 5)	%	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
TiO_2 5)	%	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03
HCl 5) 6)	%	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.05	≤ 0.05	≤ 0.02	≤ 0.025	≤ 0.025

The data represents non-binding typical values

DDS = dimethyldichlorosilane
D4 = octamethylcyclotetrasiloxane
HMDS = hexamethyldisilazane

Table 3
Typical physico-chemical data for AEROXIDE®

		AEROXIDE®	
		TiO_2 P 25	TiO_2 PF 2
Surface modification		None, hydrophilic	None, hydrophilic
BET surface area 1)	m^2/g	50 ± 15	57 ± 13
pH 2)		3.5–4.5	3.5–4.5
Tamped density 3) (approximate value)	g/l	130	80
Compacted material with higher tamped density available on request?		No	No
Loss on drying 4) (2 h at 105 °C)	%	≤ 1.5	≤ 2.0
SiO_2 5)	%	≤ 0.2	–
Al_2O_3 5)	%	≤ 0.3	–
TiO_2 5)	%	≥ 99.5	≥ 94.0
HCl 5) 6)	%	≤ 0.3	–
Fe_2O_3	%	–	2 ± 1.0

The data represents non-binding typical values

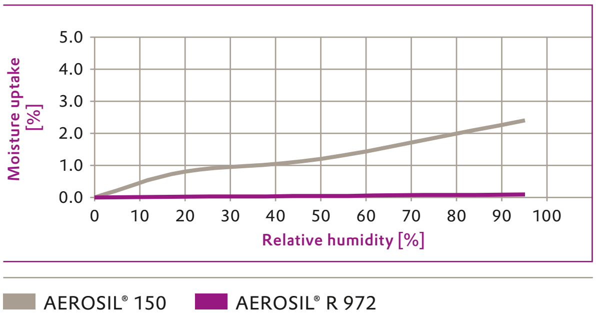
1) Based on DIN ISO 9277
2) Based on DIN EN ISO 787–9, ASTM D 1208, JIS K 5101/26
3) Based on DIN EN ISO 787–11, JIS K 5101/20 (not sieved)
3) VV products are currently supplied exclusively from the Rheinfelden site
4) Based on DIN EN ISO 787–2, ASTM D 280, JIS K 5101/23
5) For the substance ignited for 2 hours at 1000 °C
6) HCl content is part of the ignition loss.

3. Hydrophilic and hydrophobic fumed silica for RTV-1 Silicone Sealants

Silanol and siloxane groups are present on the surface of untreated AEROSIL® fumed silica. This makes the AEROSIL® hydrophilic, or have a high affinity to water and it can be wetted by water completely. AEROSIL® 150, for example, is capable of adsorbing considerable amounts of water.

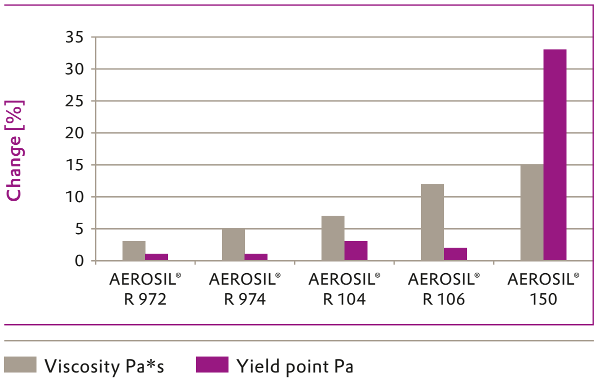
The reaction of the silanol groups with organic silicone compounds results in alkyl silyl groups being chemically anchored on the surface. The resulting products are hydrophobic, i.e. are not wetted by water and absorb only very small amount of it. These products carry the suffix R (R stand for "repellent"), for example, AEROSIL® R 972. The ability of moisture uptake of hydrophilic AEROSIL® 150 and hydrophobic AEROSIL® R 972 can be demonstrated in Figure 2. The hydrophobic fumed silica grades which are most commonly used in the silicone industry are listed below (see box), in order of increasing level of hydrophobicity.

Figure 2
Moisture uptake of AEROSIL® 150 and AEROSIL® R 972



In RTV-1 Silicone Sealants the thickening action of fumed silica decreases with the degree of hydrophobization. Typically, higher levels of hydrophobicity result in lower thickening. However, concerning dispersibility, the more strongly hydrophobized the silica, the more easily it incorporates and disperses into formulations. Another advantage of hydrophobic fumed silica in a RTV-1 Silicone Sealants formulation is the improvement of storage stability. This can be seen in Figure 3, showing the percent change in viscosity and yield point of 1-component RTV alkoxy sealant compound after storage for 56 days at 50 °C. In moisture-sensitive RTV–1 formulations, hydrophobic fumed silica is preferred because of its low moisture content and negligible moisture uptake during storage.

Figure 3
Percentage change in viscosity and yield point of a RTV-1 alkoxy sealant compound after storage for 56 days at 50 °C



The hydrophobic fumed silica grades which are most commonly used in the silicone industry, in order of increasing level of hydrophobicity

AEROSIL® R 974 ≤ AEROSIL® R 972 < AEROSIL® R 104 ≤ AEROSIL® R 106 < AEROSIL® R 812 S

4. Options for adjusting the properties of RTV-1 Silicone Sealants

In RTV-1 Silicone Sealants, the properties such as thickening impact, mechanical strength, expansion behavior and transparency can be controlled by proper selections of hydrophilic and hydrophobic fumed silica.

The plot between the degree of hydrophobization versus the BET surface area of various AEROSIL® grades is shown in Figure 4. Figure 5 – 7 present the individual property that can be selectively controlled by changing the surface area or the degree of hydrophobization.

In general, the following statements can be applied for RTV-1 Silicone Sealants formulations for any changes in the surface area or in the degree of hydrophobization of the fumed silica used:

As the surface area increases ...

- the thickening impact increases and the increase in the reinforcing properties is noticeable. This allows a reduction in the amount of the reinforcing filler used.
- hydrophilic silica in RTV-1 Silicone Sealants are more difficult to incorporate and disperse.
- silicone sealant compounds with higher transparency can be produced.

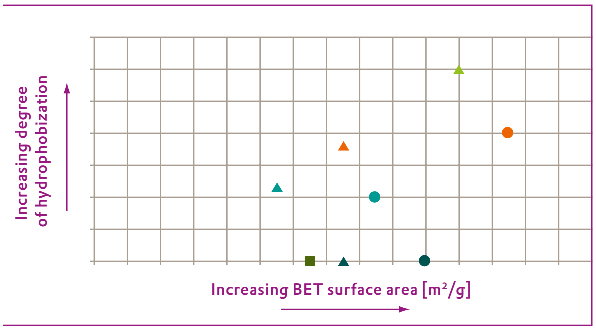
By hydrophobizing fumed silica ...

- water uptake is significantly reduced, resulting in improved storage stability of moisture sensitive RTV–1 Silicone Sealant formulations.
- incorporation behavior and dispersibility are significantly improved.
- the amounts of crosslinkers and water scavengers used in RTV-1 Silicone Sealants can be reduced, resulting in reduced raw material costs.

With an increasing degree of hydrophobicity ...

- lower viscosities are obtained in RTV-1 Silicone Sealants.
- mechanical properties are changed only slightly.
- greater freedom is possible in formulation.

Figure 4
Degree of hydrophobization and BET surface area of various AEROSIL® grades



- ■ AEROSIL® 130
- ▲ AEROSIL® 150
- ● AEROSIL® 200
- ▲ AEROSIL® R 972
- ● AEROSIL® R 974
- ▲ AEROSIL® R 104
- ● AEROSIL® R 106
- ▲ AEROSIL® R 812 S

Figure 5
Viscosity of different RTV-1 Silicone Sealants formulated with various AEROSIL® grades.
(acetoxy sealing compounds, 8 % filler content)

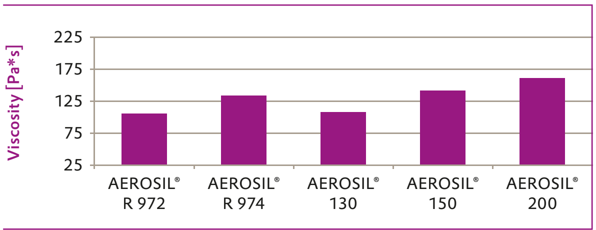


Figure 6
Modulus 100% of different RTV-1 Silicone Sealants formulated with various AEROSIL® grades
(acetoxy sealing compounds, 8 % filler content)

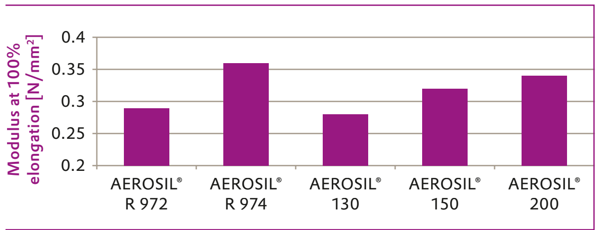
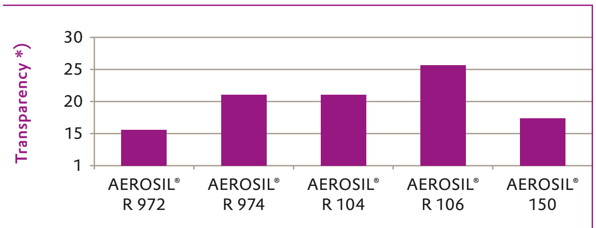


Figure 7
Transparency of different RTV-1 Silicone Sealants formulated with various AEROSIL® grades
(acetoxy sealant compounds, 8 % filler content)



*) Higher values indicate greater transparency

5. AEROXIDE® heat stabilizers for high temperature applications

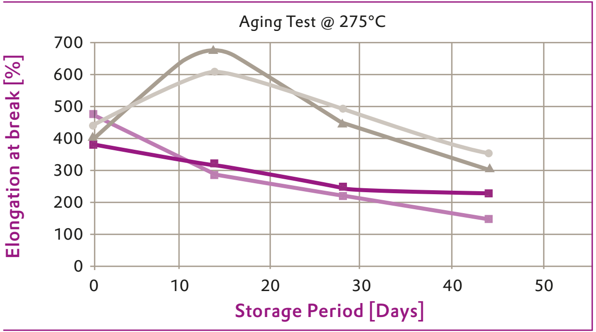
Silicone sealant compounds are elastomers, whose physical and mechanical properties can be changed only slightly under thermal stress. The reason for the high thermal resistance is due to the stable Si-O-Si framework. Severe degradation of the silicone polymers occurs only at temperatures above about 200 °C. At high temperature changes can occur essentially in two ways:

- Atmospheric oxygen causes decomposition of the organic groups. This oxidation leads to the breakdown of the polymer with formation of volatile products via an embrittlement or gel phase.
- In the absence of atmospheric oxygen, particularly under the catalytic action of acids and bases, depolymerization occurs, leading to formation of low-molecular siloxanes.

Only at temperatures above about 450 °C, the pyrolytic degradation of the silicone polymers occurs, with the formation of silica, carbon dioxide and water.

Addition of the fumed iron-titanium mixed oxide, AEROXIDE® TiO_2 PF 2, or of the fumed titanium oxide, AEROXIDE® TiO_2 P 25, results in heat stabilization due to the oxidizing properties of the metal ions. Electrons can be taken up, so that the free radicals formed by thermal stress on the polymer are rendered innocuous. Uncontrolled polymerizations and oxidation reactions are greatly inhibited.

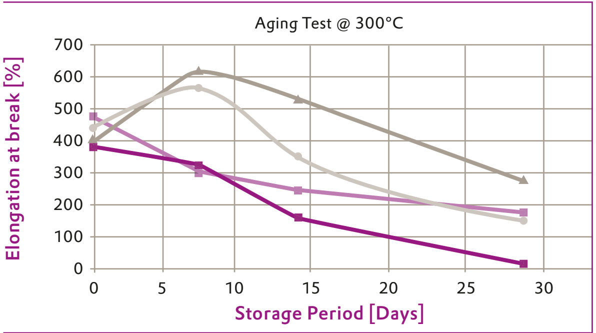
Figure 8
Elongation at break (%) of RTV-1 Silicone Sealants containing different heat stabilizer after storage at 275 °C, 42 days, compared with a market sample



- 1.5% AEROXIDE® TiO_2 P 25
- 3% AEROXIDE® TiO_2 P 25
- 1.5% AEROXIDE® TiO_2 PF 2
- Market Sample (iron oxide red)

75 – 85% Silicone Polymer
5 – 10% Silicone Oil
4 – 6% Crosslinker
1% Adhesion Promoter
0.01% Accelerator
8 – 10% Fumed Silica
0.5 – 10% Heat Stabilizer

Figure 9
Elongation at break (%) of RTV-1 Silicone Sealants containing different heat stabilizer after storage at 300 °C, 28 days, compared with a market sample



- 1.5% AEROXIDE® TiO_2 P 25
- 3% AEROXIDE® TiO_2 P 25
- 1.5% AEROXIDE® TiO_2 PF 2
- Market Sample (iron oxide red)

75 – 85% Silicone Polymer
5 – 10% Silicone Oil
4 – 6% Crosslinker
1% Adhesion Promoter
0.01% Accelerator
8 – 10% Fumed Silica
0.5 – 10% Heat Stabilizer

6. Dynasylan® silane as adhesion promoter

When used as an adhesion promoter, Dynasylan® acts as a bifunctional organosilicon compound, producing a chemical bond or interaction between a silicone sealant and the inorganic or organic substrate. For adhesion promotion, Dynasylan® can be used directly as an additive in the production of a RTV-1 Silicone Sealants. For particularly complicated adhesion problems, Dynasylan® can also be applied on the substrate as a primer in aqueous or solvent-containing form.

Figure 10
Mechanism of adhesion promotion

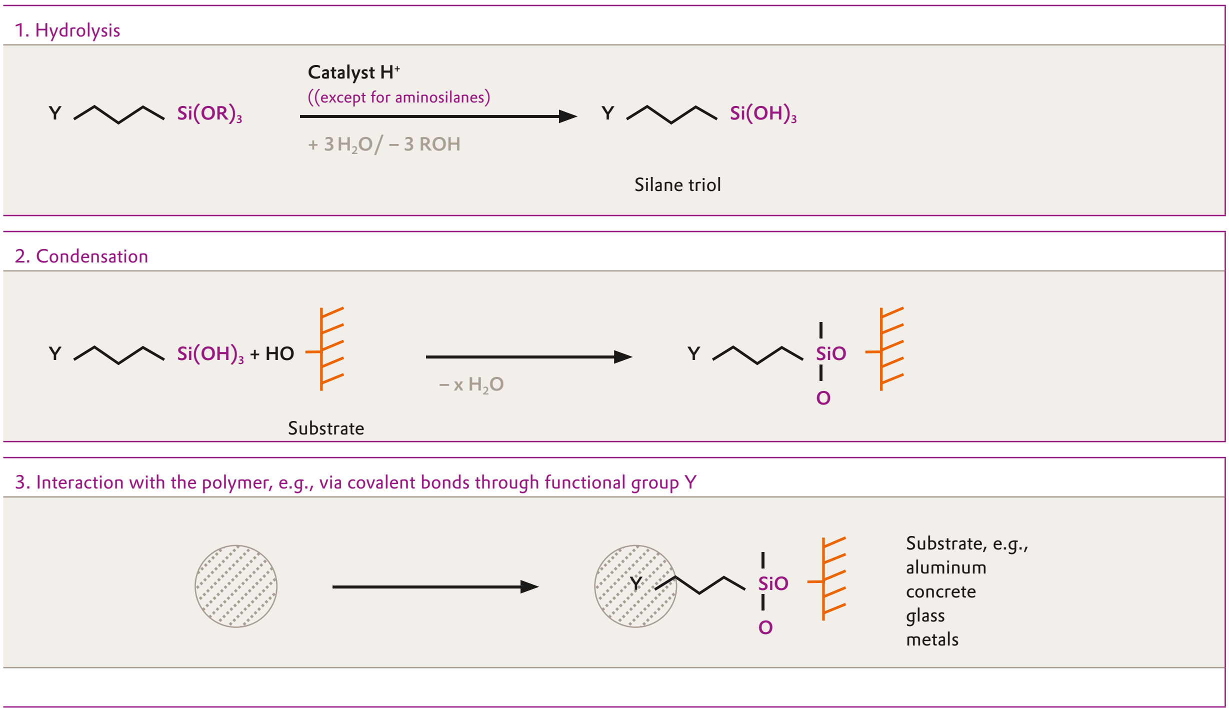


Table 4
Product recommendations, according to the types of RTV–1 silicone systems

RTV silicone type	Organofunctional silane	Chemical structure
Alkoxy systems	Dynasylan® TRIAMO	Triamino functional propyltrimethoxysilane
	Dynasylan® AMEO	Aminopropyltriethoxysilane
	Dynasylan® DAMO-T	Diamino functional propyltrimethoxysilane
	Dynasylan® 1146	Amino functional silane oligomer
Acetoxy systems	Dynasylan® BDAC	Di-t-butoxydiacetoxysilane
Oxime systems	Dynasylan® AMEO	Aminopropyltriethoxysilane
	Dynasylan® DAMO-T	Diamino functional propyltrimethoxysilane
	Dynasylan® TRIAMO	Triamino functional propyltrimethoxysilane
	Dynasylan® 1146	Amino functional silane oligomer

The Dynasylan® 1146 product is particularly distinguished because of the following advantages:

- wide adhesion spectrum
- fast cure
- low tendency to yellowing
- positive influence on elasticity
- reduced VOC content

7. Dynasylan® silane as crosslinker

Dynasylan® organofunctional silane can be used as crosslinkers RTV-1 Silicone Sealants by condensation reactions by which the properties such as elastic modulus, elongation, and tensile strength are positively influenced. The tri- or tetrafunctional silane reacts with the end groups of the oligo siloxanes to give the functionalized organopolysiloxane chains as seen in Figure 11. During processing, these functional polysiloxane chains are crosslinked by the action of atmospheric humidity to provide a crosslinked (elastic) silicone polymer as shown in Figure 12.

Figure 11
Example of the reaction of functionalization of a silicone polymer

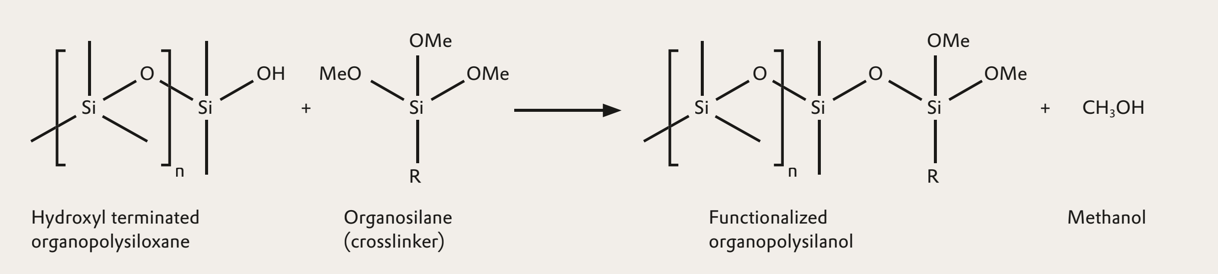


Figure 12
Example of a crosslinking reaction in the presence of moisture to provide a crosslinked (elastic) silicone polymer

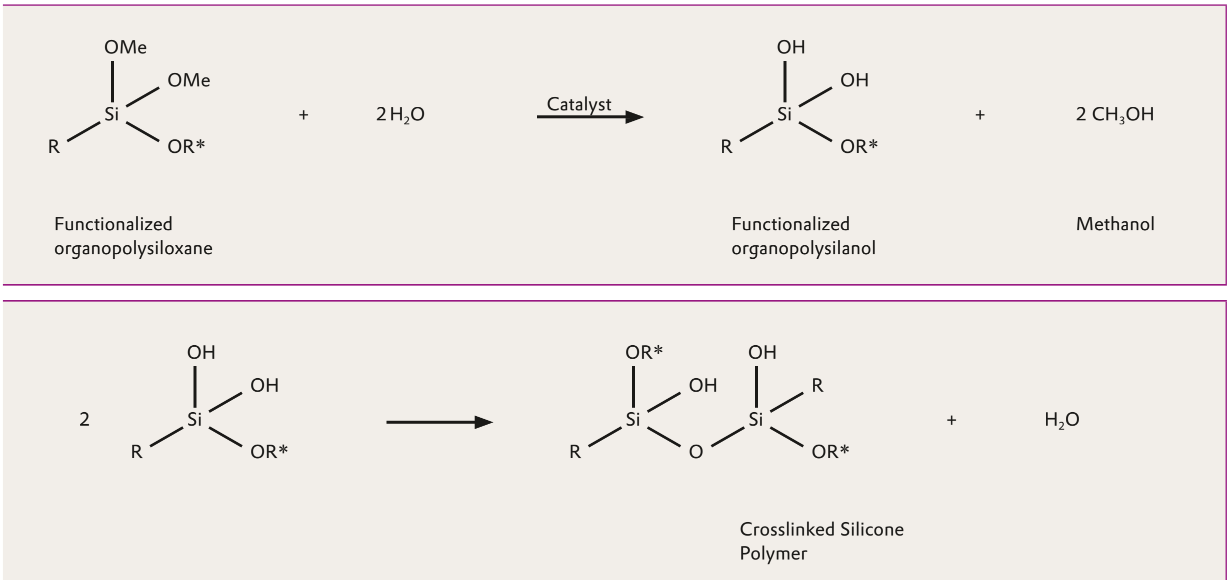


Table 5
Product recommendations for RTV–1 alkoxy systems

RTV silicone type	Organofunctional silane	Chemical structure
Alkoxy systems	Dynasylan® A	Tetraethoxysilane
	Dynasylan® P	Tetra-n-propoxysilane
	Dynasylan® 40	Ethylpolysilicate
	Dynasylan® VTMO	Vinyltrimethoxysilane

8. Testing Formulation

8.1. Acetoxy Formulation

62.4 % of Silicone Polymer (Polymer OH 50/ Evonik Hanse GmbH)

24.6 % of Silicone Oil (Siliconöl M1000/ Momentive Performance Materials)

4.0 % of Crosslinker (Crosslinker AC 10; Evonik Hanse GmbH)

1.0 % of Coupling Agent (Dynasylan® BDAC/ Evonik Industries AG)

0.01 % of Catalyst (dibutyltin diacetate/ TIB Chemicals)

8.0 % of Fumed Silica (AEROSIL® 150/ Evonik Industries AG)

8.2. Alcoxy Formulation

80.0% of Silicone Polymer (Polymer OM 23/ Evonik Hanse GmbH)

10.0 % of Silicone Oil (M1000/ Momentive Performance Materials)

2.0 % of Ahdesion Promoter (Dynasylan® 1146/ Evonik Industries AG)

8.0 % of Fumed Silica (Evonik Industries AG)

0.07 % of Catalyst (Catalyst TK 14/ Evonik Hanse GmbH)

9. Literature

Product Overview
- AEROSIL® Product Overview
- Dynasylan® Product Range

Industry Brochure Adhesives & Sealants
- AEROSIL® and Silanes for Adgesives & Sealants

Technical Bulletin No. 28
- Handling of synthetic silica and silicate

Technical Information No. 1148
- AEROSIL® R 104 and AEROSIL® R 106 for silicone rubber applications

Technical Information No. 1209
- AEROSIL® R 8200 for silicone rubber

Technical Information No. 1218
- AEROXIDE® TiO_2 P 25 and AEROXIDE® TiO_2 PF 2 Effective Heatstabilizers for Silicone Rubber

Technical Information No. 1253
- AEROSIL® and AEROXIDE® for Liquid Silicone Rubber

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