

AEROSIL[®] fumed silica and SIPERNAT[®] in sealants

Technical Bulletin Fine Particles 63



Sealants based on polysiloxanes, polyurethanes or polyacrylates steadily have been gaining importance over the last few years. Today's design technology would be unimaginable without the use of such substances, since more and more combinations of materials are being joined and sealed for economic and technical purposes.

For many years now, synthetic silicas from Evonik Industries have helped to modify the properties of modern sealants and to improve them for specific applications. In many cases (e.g. polysiloxanes), it would be quite inconceivable not to use synthetic silicas, because these are largely responsible for the mechanical strength of the vulcanized materials.

This publication in the Technical Bulletin series summarizes the fundamental features of the highly dispersed silicas which are suitable for use in modern sealants. Their wide-ranging potential will be examined in detail from the point of view of application technology.

*Rüdiger Nowak
Uwe Schachtely*

Evonik Resource Efficiency GmbH
Applied Technology

Table of Contents

	Page
1	Introduction _____ 5
2	Synthetic Silicas for Sealants _____ 5
2.1	Hydrophilic Silicas _____ 6
2.1.1	Standard AEROSIL® Products _____ 6
2.1.2	Precipitated Silicas _____ 6
2.2	Hydrophobic Silicas _____ 6
2.2.1	AEROSIL® „R Types“ _____ 6
2.2.2	Precipitated Silicas, hydrophobic _____ 7
2.3	Guide of Individual Silica Types for the Various Sealants _____ 7
3	Sealant Classification According to Properties and Raw Material Basis _____ 8
3.1	Elastic Sealants _____ 8
3.1.1	Silicone Rubber Sealants _____ 9
3.1.2	Polysulphide Sealants _____ 10
3.1.3	Polyurethane Sealants _____ 10
3.2	Plastic Sealants _____ 11
3.2.1	Polyacrylate Sealants _____ 11
3.2.2	Butyl Rubber/Isobutylene Sealants _____ 11
3.3	Polyvinyl Chloride Sealants _____ 12
4	Theoretical Background on the Effects of AEROSIL® Fumed Silica and Precipitated Silicas as Active Fillers in Sealants _____ 13
4.1	Reinforcement of Elastomers _____ 13
4.2	Rheological Changes _____ 13
4.3	Mechanism of Reinforcement and Rheological Change _____ 13
5	Properties of Formulations Based on AEROSIL® Fumed Silica and Precipitated Silicas _____ 14
5.1	Silicone Rubber Sealants _____ 14
5.1.1	Influence of the BET Surface of AEROSIL® Fumed Silica _____ 15
5.1.2	Influence of the AEROSIL® Fumed Silica Concentration _____ 16
5.1.3	Influence of the Hydrophobicity of AEROSIL® Fumed Silica _____ 16
5.1.4	Shelf Life of Silicone Sealants _____ 17
5.1.5	Which AEROSIL® Fumed Silica for which Properties? _____ 18
5.1.6	Effect of Formula Constituents on the Properties of Silicone Sealants _____ 18
5.2	Polysulphide Sealants _____ 19
5.2.1	Comparison of AEROSIL® Fumed Silica and Precipitated Silicas _____ 19
5.2.2	Rheological Properties of AEROSIL® Fumed Silica and Precipitated Silicas _____ 19
5.2.3	Storage Stability _____ 20
5.2.4	Reinforcing Properties of AEROSIL® Fumed Silica and Precipitated Silicas _____ 21
5.3	Polyurethane Sealants _____ 22
5.3.1	Particularly Suitable Silicas _____ 22
5.3.2	Rheological Properties of Hydrophilic and Hydrophobic AEROSIL® Types _____ 22
5.4	Polyvinyl Chloride Sealants _____ 23
5.4.1	Significance of AEROSIL® Fumed Silica _____ 23
5.4.2	Influence of the BET Surface _____ 24
5.4.3	Storage Stability _____ 24
5.5	Polyacrylate Sealants _____ 24

	Page
6	General Aspects of the Dispersibility of Silicas _____ 25
7	Description of Certain Specific Test Methods _____ 26
7.1	Extrudability _____ 26
7.2	Sag Behaviour _____ 26
7.3	Measuring Thixotropy _____ 26
7.3.1	Thixotropic Index _____ 27
7.3.2	Thixotropic Area _____ 27
7.3.3	Viscosity/Time Graphs _____ 27
8	Testing and Guide Formulations _____ 28
8.1	Testing Formulations _____ 28
8.2	Guide Formulations _____ 28
8.3	List of Suppliers _____ 30
9	Product Safety Aspects for the Handling of Synthetic Silicas _____ 30
10	References to Published Sources _____ 31
11	Physical and Chemical Data of AEROSIL® Fumed Silica _____ 32
12	Physical and Chemical Data of SIPERNAT® Precipitated Silica _____ 34

1 Introduction

Sealants have assumed an increasingly significant role in large-scale and light industrial practice. In consequence, the demand for and consumption of these substances is steadily increasing. In various countries, the term „sealant“ to be defined in section 3 – overlaps in terms of its application both with adhesives and with products from the paint industry. It is therefore difficult to obtain precise production or consumption statistic especially as there are problems associated with classifying them in terms of primary chemicals.

2 Synthetic Silicas for Sealants

Synthetic silicas are produced industrially by various processes. Dating back to 1968, they are classified according to the production process into pyrogenic or thermal products, silica products based on the wet process, and aftertreated products (1); they were classified more precisely in 1976 (2). This classification makes it easier, on the one hand, to identify wellknown commercial products and on the other, to understand their often extremely varied behaviour – cf. Publication No. 32 in the Pigments Technical Bulletin series. Evonik Industries principal production methods for synthetic silicas are the AEROSIL® fumed silica and precipitation processes (Table 1). These processes can be used to obtain specifically designed products for a wide variety of applications.

Table 1 Comparison of AEROSIL® fumed silica and precipitation processes

Pyrogenic
AEROSIL® process $\text{SiCl}_4 + 2 \text{H}_2 + \text{O}_2 \xrightarrow{>1000^\circ\text{C}} \text{SiO}_2 + 4 \text{HCl}$ <i>Silicon tetrachloride</i>
Wet
precipitation process $\text{Na}_4\text{O} \times 3.3 \text{SiO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\text{Stirred}} 3.3 \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ <i>(Sodium silicate)</i>

The AEROSIL® process was developed by Evonik, and a patent was applied for, in 1941 (3, 4). It was originally conceived as a basis for producing „white carbon black“ instead of black activated fillers. But it was quickly noticed that AEROSIL® fumed silica possessed universal properties which were not just limited to an excellent reinforcing action. The rheological properties of sealants can also be systematically modified by means of AEROSIL® fumed silica. The commercial name „AEROSIL“ is a registered trademark in many countries.

In addition to Germany, AEROSIL® fumed silica is currently manufactured in Belgium, Japan, the USA and France. The AEROSIL® process is also suitable for producing other pyrogenic oxides such as titanium oxide or aluminium oxide. Issue No. 56 of the Technical Bulletin series describes these products in more detail. Synthetic silicas are largely responsible for enhancing the mechanical strength of elastic sealants, i.e. those with a chemical crosslinking action. They are also used to adjust the flow properties of sealants in order to form stable, pastelike products. For this purpose, the main focus is on synthetic silicas produced according to the AEROSIL® and precipitation processes. Evonik manufactures both types of silica and supplies appropriate products for specific applications.

2.1 Hydrophilic Silicas

2.1.1 AEROSIL® Products

AEROSIL® fumed silica is a very light, bluish-white powder formed from very fine, spherical primary particles. Although these particles are amorphous, they do not occur in isolation adjacent to one another but aggregate and agglomerate to form larger configurations. Their average diameters range from 7 to 40 nanometres. Since the particles are so small, they result in an extremely high specific surface area which is usually determined by the nitrogen adsorption method based on BRUNAUER, EMMETT and TELLER (the „BET“ method) and which, depending on production parameters, may be between 50 m²/g and 380 m²/g. The surface of AEROSIL® particles is relatively smooth, consisting of the boundary surface of a spatial network of siloxane groups (-Si-O-Si-). Silanol groups are also located on the surface of silica particles. As moisture can be adsorbed at these points, silicas such as AEROSIL® fumed silica are normally hydrophilic and hence can be wetted with water. Further details are contained in Publication No. 11 of the Technical Bulletin series. In most instances, hydrophilic AEROSIL® types with specific surfaces between 130 m²/g and 380 m²/g are used in sealants, depending on the polymer system and the desired effect.

2.1.2 Precipitated Silicas

Manufacture and properties of the various processes are described in Publication No. 32 of the Technical Bulletin series. The crucial difference between precipitated silicas and the AEROSIL® types is their purity. For example, the drying and ignition loss value of precipitated silicas, app. 5% by weight, is about three times greater than that of AEROSIL® fumed silica. The silanol-group densities in precipitated silicas are also higher than in the AEROSIL® types. Another important difference is that, because of their more pronounced agglomerate formation, most commercially available precipitated silica types are ground, whereas all AEROSIL® types are left unground.

2.2 Hydrophobic Silicas

Hydrophobic silicas are always after-treated products. Aftertreatment processes can be performed by using either the different types of AEROSIL® or the various types of precipitated silicas.

2.2.1 AEROSIL® „R Types“

AEROSIL® R 972 has been commercially available since 1962 and is the oldest chemically aftertreated synthetic silica, i. e. the first hydrophobic product on the market. Unlike silicas which are naturally hydrophilic, hydrophobic types are not wetted by water. Although the hydrophobic silicas' density is greater than water, they float on the surface of water.

In the case of AEROSIL® R 972, chemically bonded dimethyl silyl groups are produced at the silica surface as a result of binding the hydrophilic silanol groups with dimethyl dichlorosilane. Other hydrophobic AEROSIL® types have now become available commercially and are designated by an „R“. This „R“ stands for „repellent to water“. They differ in their specific surface area and the organic groups located on the silica surface. AEROSIL® R 974 differs from AEROSIL® R 972 by virtue of its higher BET surface.

In terms of the geometrical surface area, AEROSIL® R 812 can be compared with AEROSIL® 300, but has trimethyl silyl groups on the silica surface. In principle, every hydrophilic AEROSIL® type can be modified by dimethyl silyl or trimethyl silyl groups. Appropriate test products were also produced for comparison purposes. Of all the hydrophobic AEROSIL® types, AEROSIL® R 202 has the lowest BET surface of 100 m²/g and is after-treated with a polydimethyl siloxane. AEROSIL® R 805 is rendered hydrophobic by means of a silane with a fairly long chain organic group, e.g. an octylsilane. Hydrophobizing substantially reduces the amount of moisture that is absorbed by hydrophilic silicas, cf. **Figure 1**. For example, AEROSIL® R 974, even at a relative air humidity of 80 %, adsorbs just 0.5% water, whereas the hydrophilic AEROSIL® 200 with a comparable surface area absorbs some 10 times more.

Figure 1 Moisture adsorption isotherms at room temperature of AEROSIL® 200 and AEROSIL® R 974, measured on small specimens.

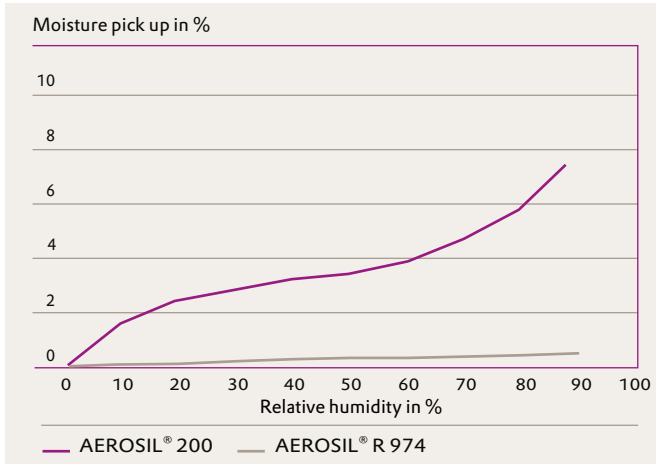
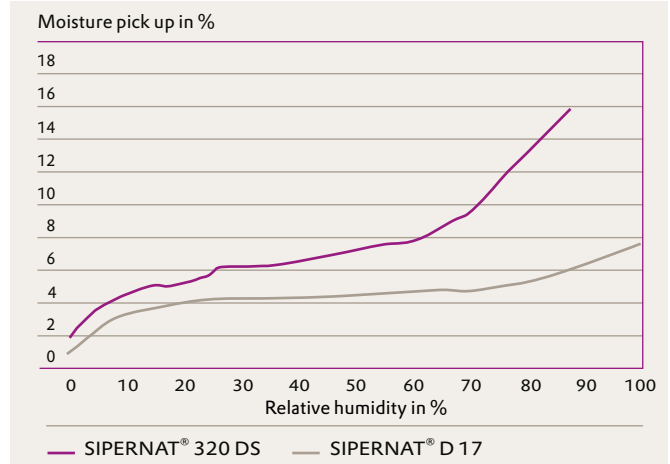


Figure 2 Moisture adsorption isotherms at room temperature of SIPERNAT® 320 DS and SIPERNAT® D 17, measured on small specimens.



2.2.2 Precipitated Silicas, Hydrophobic

In principle, all the general data on AEROSIL® “R types” also apply to hydrophobic precipitated silicas. As is shown in Figure 2 which compares the water adsorption isotherms of precipitated silica SIPERNAT® 320 DS and SIPERNAT® D 17 (hydrophobic), the moisture adsorption is considerably reduced by chemical after-treatment. But it is evident from examination of the precipitated silica that it was produced by a wet process, exhibiting characteristics differences with AEROSIL® types as already dis-

cussed in 2.1 – Hydrophilic silicas. The hydrophobic precipitated silica SIPERNAT® D 10 has proved to be a suitable reinforcing filler and thixotropic agent for polysulphide sealants.

2.3 Guide of Individual Silica Types for the Various Sealants

Table 2 contains application Information on the use and incorporating of Evonik silicas in various sealant systems.

Table 2 Recommendations for applications for AEROSIL® types and precipitated silicas.

Sealant system	AEROSIL®-Grade	Silica concentration in wt. %	Effect	Dispersion Equipment
1-K Silicone (RTV-1)	AEROSIL® 130	7–10	Anti-Sag, Thixotropy, Reinforcement, Improves Transparency (R 106, R 812 S), Self-leveling (R 8200), Thermal stability (AEROXIDE® TiO ₂ P 25)	Planetary-Dissolver, Press-Mixer, Extruder
	AEROSIL® 150	7–10		
	AEROSIL® R 972	7–10		
	AEROSIL® R 974	7–10		
	AEROSIL® R 106	7–10		
	AEROSIL® R 812 S	7–10		
	AEROSIL® R 8200	7–10		
	AEROSIL® TiO ₂ P 25	7–10		
2-K Silicone (RTV-2)	AEROSIL® TiO ₂ P 25	15–30	Reinforcement, Self-leveling, Thermal stability (AEROXIDE® TiO ₂ P 25)	Planetary-Dissolver, Press-Mixer, Kneader
	AEROSIL® R 812 S	0.5–1.5		
1-K Polyurethane	AEROSIL® R 972	2–10	Anti-Sag, Thixotropy, Anti-Settling, Reinforcement	Planetary-Dissolver, Kneader, Inline Rotor-Stator
	AEROSIL® R 974	2–10		
	AEROSIL® R 202	2–7		
Polyacrylate	AEROSIL® 200	0.8–3	Anti-Sag, Thixotropy, Reinforcement	Planetary-Dissolver, Rotor-Stator
	AEROSIL® R 972	0.8–4		
	AEROSIL® R 974	0.8–4		
	AEROSIL® R 805	0.8–4		
Polysulfide	AEROSIL® 200	1–4	Anti-Sag, Thixotropy, Reinforcement	Planetary-Dissolver, Kneader
	AEROSIL® R 972	1–4		
	AEROSIL® R 202	1–3		
	SIPERNAT® D 10	5–20		
	SIPERNAT® 383 DS	5–12		
Butyl	AEROSIL® 200	1–3	Anti-Sag, Thixotropy, Reinforcement	Planetary-Dissolver, Kneader
	AEROSIL® R 972	1–4		
MS/SMP/SPU	AEROSIL® R 972	1–4	Anti-Sag, Thixotropy, Reinforcement	Planetary-Dissolver, Kneader
	AEROSIL® R 974	1–4		
	AEROSIL® R 8200	5–15		
PVC-Plastisol	AEROSIL® 200	0.8–1.2	Anti-Sag, Thixotropy	Planetary-Dissolver, Kneader, Triple roll mill
	AEROSIL® 300	0.8–1.2		
	AEROSIL® 380	0.8–1.2		

3 Sealant Classification According to Properties and Raw Material Basis

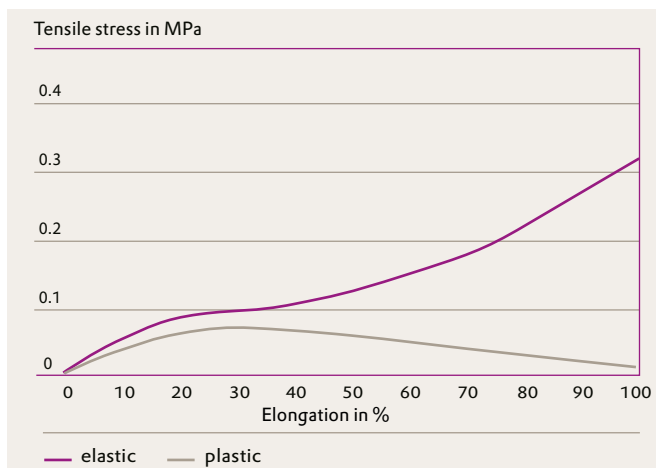
In accordance with German Industrial Standard DIN 52 460, sealants or sealing compounds are plastic substances with adhesive properties which are suitable for filling joints and cavities between two materials. After setting they adhere to the material's edges and seal the joints so as to provide protection against environmental exposure.

Modern sealing technology is based on elastomeric materials. As new elastomers continued to be developed, vulcanization and hardening systems were discovered in the 1950's and 1960's which also function effectively at room temperature. The most common sealant at that time was the so-called window or glazier's putty (oil-based putty) which was soon replaced by sealants suitable for plastic processing. The development of sealants is closely linked to that of modern adhesives. Unlike adhesives, sealants have to be able to accommodate fairly large joint movement between the material elements without suffering damage themselves.

In principle, sealants can be subdivided into two groups. A distinction is made between chemically hardening (cross-linking) systems which change into an elastic state, and physically setting systems which mostly remain in a plastic state.

Figure 3 shows that elastic sealants can adsorb greater joint movements than plastic sealants. Test values for elongation tests are not directly relatable to actual joint movement. In practice, elastic sealants may experience 10% to 25% joint movement compared to plastic sealants which experience 2% to 5% or a maximum of 10%.

Figure 3 Tensile-elongation diagram of elastic and plastic sealants



3.1 Elastic Sealants

These chemically cross-linking sealants are available as one- and two-component systems formulated from reactive, elastomeric polymers. These basic polymers are still in a liquid or paste-like state. They are modified by fillers such as synthetic silicas and if needed by plasticizers and/or additives in order to enhance the stability of the compounds. They are vulcanized by means of hardening crosslinking agents. The two systems are distinguished by the manner in which they are vulcanized.

In the case of **one-component Systems (1C)**, vulcanization or crosslinking is initiated by moisture taken from the air and/or from the substrate. The „disguised“ or „blocked“ cross-linking agent is activated by the moisture and, depending on the type of sealant, reaction products are separated and released. After a relatively short period of time, a skin forms on the surface and the cross-linking process continues from within until the sealant has completely hardened. The speed of cross-linking depends on the joint's thickness, the available moisture and the ambient temperature. The possible disadvantage of a fairly long vulcanization time is compensated by the fact that these ready-to-use sealants are easy to handle.

In the case of **two-component Systems (2C)**, the base polymers (component A), which contain fillers, are packed separately from the cross-linking agent (component B) when supplied to the user. Before processing, components A and B have to be homogenized at the specified mixing ratio. Vulcanization begins when this mixing process starts, so that the resulting compound can only be processed before a specific period of time has elapsed (pot life). The cross-linking speed does not depend here on the depth of the seal joint or the thickness of the coating.

3.1.1 Silicone Rubber Sealants

Silicone rubber or polyorganosiloxanes, to give them their more exact chemical name, are polymer compounds in the main chain of which silicon atoms are alternately linked via oxygen atoms. The remaining valencies of the silicon are saturated by organic (almost exclusively methyl) groups. The individual silicone chains are cross-linked by functional groups such as terminal silanol groups, to form elastomers. Due to their excellent properties such as high resistance to heat, flexibility at sub-zero temperatures and outstanding resistance to aging and chemicals, silicone sealants are highly versatile in their applications. 1 C systems are virtually the only ones used as silicone sealants. Quantitatively speaking, 2 C systems play only a very minor role in the production of sealants. They are more frequently used for casting and moulding compounds. These 2 C systems include those which cross-link by condensation and those which do so by addition. The 1 C systems cross-link by condensation and are also designated as 1C-RTV (= room-temperature vulcanized). The principal constituents making up a 1 C silicone sealant are base polymers, cross-linking agents, plasticizers, fillers, catalysts and special additives.

A linear polydimethylsiloxane with terminal silanol groups and a molar weight of 40,000 to 120,000 is used as a basic polymer in 1 C silicone sealants. Adding a cross-linking agent to the silanol groups at the ends of the chains produces an inactive system for as long as moisture is excluded. If atmospheric moisture is present, long chains of cross-linked polysiloxanes form.

Trifunctional silanes of the general form RSiX_3 are chiefly used as cross-linking agents for today's commercially available 1 C silicone sealants. Depending on the type of cross-linking agent used, a distinction is made between acidic, neutral and basic systems, as shown in Table 3.

Table 3 Classification of the principal cross-linking agent systems.

Cross-linking agent system	Substituent	Formula
Acidic	Acetate	$-\text{O}-\text{CO}-\text{CH}_3$
Neutral	Oxime	$-\text{NO}=\text{CR}_2$
	Benzamide	$-\text{NH}-\text{CO}-\text{C}_6\text{H}_5$
	Alkoxy	$-\text{O}-\text{R}$
Alkaline	Amine	$-\text{NH}-\text{R}$

The cross-linking agents used most frequently in Germany are alkyl triacetoxysilanes (acetate cross-linking agents), followed by alkyl triethyl methyl ketoximosilanes (oxime cross-linking agents).

The cross-linking agent's task is not only restricted to three-dimensional cross-linking of the silicone polymer in a highly elastic state. As mentioned above, the reactive terminal OH groups of the silicone polymer are also blocked by an excess of cross-linking agent when stored in moisture-free conditions. In the same way, foreign OH groups for instance in the filler or foreign moisture, are also deactivated. A substantial excess quantity of the stoichiometrically essential cross-linking agent is therefore added in practice (as much as 10% of the weight of the silicone polymer).

Plasticizers are also added as a formulation constituent. They reduce the hardness of vulcanized substances. Nonfunctional silicone oils with a viscosity of 100 to 1000 mPa s are most frequently used. These silicone oils – in an optimized quantity – can also increase the elongation at break and tear-resistance of vulcanized materials.

Reinforcing fillers represent a key constituent of all silicone rubbers, since vulcanized substances without fillers exhibit only very low mechanical strength. Apart from small quantities of lamp blacks and various metal oxides, pyrogenic silicas produced by flame hydrolysis, such as AEROSIL[®], are almost exclusively used in 1 C silicone sealants.

Most 1 C silicone sealants also need a catalyst to ensure complete vulcanization at room temperature. In practice, organo-metallic tin compounds are used for this purpose. The amount of catalyst is 0.01 - 0.5%, depending on the type of cross-linking agent. Neutral systems need a much greater quantity of catalyst than an acetate or amine system in which the acidic or basic disassociation products themselves become catalytically active to some extent.

There is also a whole array of special additives for 1 C silicone sealants with various effects. Adhesion promoters are used fairly frequently. These are usually alkoxyfunctional silanes of the $\text{X-Si}(\text{OR}_3)$ type. X may be for example: acetoxy, amino, epoxy or mercapto-functional. Other additives include colored pigments or pigment blacks to provide coloration, heat stabilizers or microbiocides to counteract bacteria and fungi. Inactive fillers such as calcium carbonate (chalk) are also used.

3.1.2 Polysulphide Sealants

Basic materials for polysulphide sealants (PSR) have for a long time been known by the trade name THIOKOL®. Polysulphide polymers are obtained by treating dichloroethyl formal (= bis-β-chloroethoxymethane) with sodium polysulphide. The molecular mass of liquid polymers is between 3,000 and 4,000. They are converted into an elastic final state by reacting with an oxidizing agent (manganese dioxide, organic or inorganic peroxides).

Polysulphide sealants are mainly used as 2-component compounds (cf. guide formula 8.2.1). In addition to liquid polysulphide, component A contains stearic acid sulphur, adhesive resin, plasticizer, neutral fillers, pigment and AEROSIL® fumed silica or precipitated silicas. The hardener component B consists of a plasticizer paste and manganese dioxide or some other hardener.

In the case of 1-component systems, the hardener (e.g. calcium peroxide or sodium perborate) is added to the sealant before it is packed. The hardening reaction does not occur in the cartridge, but only takes place after processing when atmospheric moisture has reached it (cf. guide formula 8.2.2). Unlike silicone rubber, the completely vulcanized polysulphide rubber represents an excellent water vapour barrier, so that the hardening process is a very slow one. This particular feature limits these 1-component compounds to areas in which fairly low coating thicknesses are required and where no immediate elongation or compression loads are to be expected.

Principal features of polysulphide sealants include high elongation and compression capacity (25% practical elongation absorption) and excellent resistance to ozone, water, oil, solvents and various other chemicals.

Precipitated silicas in addition to AEROSIL® types can be used for thickening and thixotropy of 1 and 2-component polysulphide sealants. After-treated silicas, which exhibit excellent non-sag properties and storage stability, have proved to be particularly successful.

3.1.3 Polyurethane Sealants

Polyurethane (PUR) sealants are marketed as 1- and 2-component products. Their significance continues to increase. They are extremely important for the direct bonding of windscreens, in expansion joints as used in building and civil engineering, and for aircraft construction and shipbuilding.

The principal features of PUR sealants include:

- excellent adhesion
- resistance to chemicals
- elasticity
- hardening at low temperatures
- resistance to hydrolysis
- minimum water absorption

The 1 C PUR sealants, like 1 C silicone systems, will only cross-link if exposed to atmospheric moisture. They also have the advantage that they can be processed easily and reliably. The hardener is incorporated as a blocked polyisocyanate in the ready-to-use mixture.

2C PUR systems cross-link after the two reactive polyol and isocyanate components have been mixed together. Polyesters and polyethers containing OH groups are used as polyol components. Polycarbonates containing hydroxyl groups have also recently been introduced to the market (5).

Generally speaking, only diphenyl methane diisocyanates (MDI) are used as an isocyanate component.

Guide formulations 8.2.3 and 8.2.4 are for 1 C and 2 C PUR sealants. Since 1-component sealants and the isocyanate component of 2-component PUR sealants are very sensitive to moisture, hydrophobic AEROSIL® types are particularly suitable for thixotropy, since their moisture absorption is extremely low.

3.2 Plastic Sealants

Plastic sealants are 1 C systems which usually harden completely in a purely physical way by evaporation of an organic solvent or water.

In the case of plastic sealant systems, the polymers are already in their final state, whereas in the case of elastic sealants the polymers are not formed until a chemical reaction takes place. Plastic sealants are predominantly used for internal joints, external joints not subjected to mechanical loads, and connecting joints.

3.2.1 Polyacrylate Sealants

In the case of sealants based on polyacrylic and polymethacrylic esters, a distinction is made between aqueous systems and those containing solvents.

For ecological reasons, aqueous systems have become extremely important for general sealing purposes. Whereas silicone, polysulphide and polyurethane sealants set by means of a chemical reaction, polyacrylate sealants reach their final functional state by simple physical drying – in other words, by evaporating of the dispersion water or solvent. They consist of an aqueous dispersion, e. g. an acrylic ester copolymer, to which special plasticizers, fine-particle fillers, pigments and thixotropic agents are added. Guide formulations 8.2.5 and 8.2.6 provide more detailed information on sealants created in this way.

Sealants based on acrylic resin solutions have such a high viscosity at room temperature that they cannot be sprayed. Before processing, these acrylic resin sealants are therefore heated to about 50 to 60 °C in an incubator so that their viscosity is lowered and they become easy to spray. Hydrophilic AEROSIL® types with specific surface areas of 200 m²/g and 300 m²/g yield sufficient stability in these systems. Hydrophobic AEROSIL® types should be used whenever the sealants are to exhibit considerable water-repellent properties. Different shades of grey and black can be achieved by adding titanium oxide and lamp black.

3.2.2 Butyl Rubber/Isobutylene Sealants

Butyl rubber sealants consist of a high-molecular butyl rubber (i. e. a copolymer comprising 98 % isobutylene and 2 % isoprene) as a binding agent, plasticizers, adhesive resins, fillers, pigments and small quantities of solvents.

As plastic sealants, their excellent resistance to chemicals, weathering, heat and ozone means that they have a relatively large range of applications compared with other types of sealant. They are also used in the production of insulating glass, since their permeability to gas is much better than that of other polymers (6).

To improve adhesion, polar or „adhesive“ resins are added to butyl rubber, which does not possess any polar groups. Tests have shown that hydrophilic AEROSIL® types render butyl rubber sealants containing polar resins effectively thixotropic, while providing storage stability. Butyl rubber sealants are physically dried and hardened by evaporation of the solvents. This process may last several months. Shrinkage resulting from evaporation of the solvents may be up to 20 %.

However, there are also solvent-free butyl rubber sealants, of which the surfaces are dried with small quantities of oils which dry by oxydation. As the permanent extensibility of butyl rubber sealants varies from approx. 5 to 7 % (the value is somewhat higher for acrylic resin sealants), these plastic sealants are not used for true expansion joints. They have however proved very successful for connecting joints.

3.3 Polyvinyl Chloride Sealants

Polyvinyl chloride (PVC) sealants are chiefly used in the automobile industry as adhesive and sealant systems for beaded-edge seams on doors, engine hoods, luggage-compartment lids and as an underseal.

PVC sealants are paste-like, solvent-free, self-adhesive PVC plasticizer mixtures (so-called PVC plastisols) (7), which are hardened at increased temperatures (cf. test formula 8.1.5).

The influence of heat causes the primary PVC particles to absorb plasticizers and to swell; at 160°C gelation occurs and the PVC particles melt. On cooling, the melt solidifies into a flexible polymer matrix.

The rheological properties can be systematically adapted by means of high-surface hydrophilic AEROSIL® types. PVC plastisols have sufficient pseudoplasticity for them to be fed through pipes, but are sufficiently thixotropic for them not to be exuded from joints if the viscosity drops temporarily as a result of heating during the pregelation phase.

The mechanical properties of elastomers and cross-linked sealants are considerably enhanced by active fillers such as AEROSIL® and precipitated silicas. The rheological properties of non-cross-linked sealants are also influenced considerably by these active fillers. The effective mechanism of the silicas is identical in each instance, with viscoelastic deformation as the reinforcing or thickening process takes place. In the case of cross-linked sealants, the elastic deformation clearly predominates, whereas in the non-crosslinked state, the viscous flow characteristics are modified.

4 Theoretical Background on the Effects of AEROSIL® Fumed Silica and Precipitated Silicas as Active Fillers in Sealants

4.1 Reinforcement of Elastomers

First of all, let us define the term „reinforcement“ more precisely. It generally refers to the improvement of mechanical properties such as the tension, elongation at break, tensile strength, tear resistance and elasticity of vulcanized products. As reinforcement does not refer only to a single mechanical property such as tensile strength, it is clearly rather difficult to define. Published sources contain various definitions (8, 9, 10); Kraus' definition, which is very general and comprehensive in scope, appears to be the most appropriate (11):

„In the broadest sense, reinforcement is the change in viscoelastic properties and the rupture properties of a network with positive consequences for the product's features, without any reduction in reversible elongation.“

Today, theoretical principles for reinforcing elastomers by means of active fillers are relatively well known and described in publications on general rubber technology (12). It should be borne in mind, however, that the reinforcing effect or mechanism only applies to a system's rubber-elastic and liquid states – i. e. above the glass transition temperature T_g . As already mentioned above, the reinforcing filler's physical and chemical properties affect both the mechanical (rubberelastic states) and the rheological properties (liquid states, see 4.2).

When a mechanical load is applied to a vulcanized rubber product, various forces act upon it. The reinforcing filler is responsible for absorbing and transferring as many of these forces as possible. The extent to which the filler can perform this task effectively depends on the filler's shape, particle size and surface energy. These three factors will be described in greater detail in section 4.3, as they considerably influence the reinforcing effect.

4.2 Rheological changes

Active fillers such as AEROSIL® fumed silica and precipitated silicas are very important for improving the mechanical properties, but cannot be added in unlimited quantities. They may affect the rheological behaviour of sealants to a considerable degree. As the filler content increases, viscosity rises and flow limits are observed. A sealant's flow limit is a direct gauge of its stability and to a certain extent is important for its practical applicability. However if the degree of filling is too high, the compound can only be processed to a certain extent because of its high viscosity.

4.3 Mechanism of Reinforcement and Rheological Change

In principle, the same effects hold true for a system's reinforcing property in the rubber-elastic state and for its thickening effect in the liquid state, based on high-surface fillers such as AEROSIL® fumed silica or precipitated silicas, since both systems are above the glass transition temperature T_g .

It must be remembered, however, that unlike the reinforcing effect during the thickening process, interactive filler/filler forces play a crucial part in addition to interactive filler/polymer forces. These forces can lead to the system's flow limit (stability) being reached, solely by building up a three-dimensional network.

5 Properties of Formulations Based on AEROSIL® Fumed Silica and Precipitated Silicas

A filler's shape, particle size and surface energy determine the quality of its reinforcing or thickening effect. These three factors will now be described at greater length.

Geometrical shape of the filler particles. In the case of synthetic silicas, this shape is a result of various kinds of branched structures formed by aggregated primary particles. The void spaces are designated as stagnant volume. The amount of polymer located in this volume is no longer available to the liquid phase as a „lubricating film“ between the filler particles.

The particle size, in other terms the effective surface area of a filler (described also as extensity factor in the literature), determines the number of adhesive points (potential for interactive forces) that are possible between polymer and filler and between the filler particles. If dispersion is inadequate, a specific surface area that is too large can only be wetted to a certain extent, thereby prompting a reduction in mechanical strength and a change in the thickening effect. But if there is too much dispersion, the geometrical shape of the filler particles may be adversely affected. However, this is relatively unlikely in the production of sealants.

The surface energy of a filler affects directly the specific binding strength value for the interactive forces between polymer and filler surface and between the respective filler particles, which can be visualised in the model as a three-dimensional network. The influence of the surface energy is described also as intensity factor (12). In terms of the polymer, these interactive forces may be influenced by all the liquid constituents in the formula. In terms of the filler, they are affected by the filler's surface energy, i.e. its chemical and physical surface properties. This surface energy can be considerably influenced by rendering the silicas hydrophobic. It is also necessary to bear in mind that too high a surface energy may adversely affect dispersibility.

Theoretical principles concerning the reinforcing property and the rheological behaviour of active fillers were described in the previous section. Accurate predictions regarding the characteristics exhibited by sealants produced using AEROSIL® fumed silica and precipitated silicas are difficult, however, reinforcing and rheological properties are influenced to a considerable degree by the formula's constituents. The characteristics of these fillers will therefore be explained by drawing on the examples from several simple test formulations.

5.1 Silicone Rubber Sealants

In the case of silicone-based RTV-1 sealants, AEROSIL® fumed silica is used not only to convert the free-flowing basic substances into a stable paste form, but also to give vulcanized products sufficiently high mechanical strength. It is not possible to use precipitated silicas because of their high moisture content. Today the manufacturers of silicone sealants have their own know-how for modifying the properties of final products by means of appropriate versions of the formula or process (additive sequence, mixing units). As far as possible, therefore, a simple test formula was chosen for the following tests in order to identify the effect of silicas on product characteristics (Table 4):

Table 4 Formulation and production of a RTV-1 sealant.

Formulation (750 g preparation):	
62.4 % Silicone polymer	Silopren E 50
24.6 % Silicone oil	Silicone oil M 1000
4.0 % Acetate cross-linking agent	Ethyltriacetoxysilan
1.0 % Adhesion promoter	Dynasytan® BDAC
0.01 % Catalyst	Dibutyl tin diacetate
8.0 % Pyrogenic silica	AEROSIL® fumed silica

Silicone polymer, silicone oil, cross-linking agent and adhesion promoter are homogenized for 1 minute in a 1.5 l planetary dissolver. The silica is then incorporated and dispersed for 5 minutes in a vacuum (100 rpm mixer, 2000 rpm dissolver). After the catalyst has been added, dispersion takes place for another 5 minutes in a vacuum. The finished compound can then be filled into cartridges or tubes.

5.1.1 Influence of the BET Surface of AEROSIL® Fumed Silica

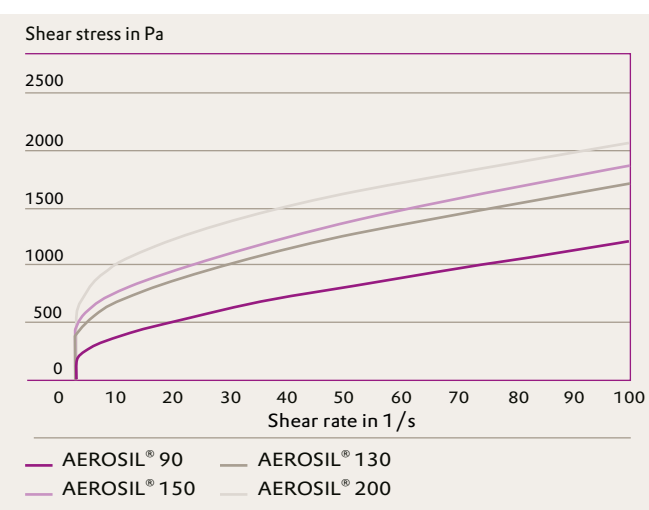
To describe the influence of AEROSIL® fumed silica on the properties of 1C silicone sealants, the BET surface was first varied in the basic experiments. As an initial test result, **Table 5** shows the properties of a silicone compound which has not been cross-linked.

Table 5 Properties of non-cross-linked silicone sealant as a function of the BET surface of AEROSIL® fumed silica

AEROSIL® fumed silica	90	130	150	200
Extrudability [g/min]	42.0	27.5	26	23.5
Viscosity [Pa s] at 10s ⁻¹	120	165	190	205
Flow limit [Pa]	180	370	410	485
Dispersion quality [Note]	2.5	2.5	2.0	3.0
Transparency [ΔE]	13.5	19	21.5	25.5

The rheological properties are particularly interesting. As the BET surface rises, the thickening effect of AEROSIL® fumed silica increases and the silicone compound's extrudability drops as a result of the higher viscosity and flow limit. The flow curve pattern in **Figure 4** also illustrates this tendency. Higher surface area grades typically require more dispersion energy. Optimum dispersion quality was obtained for this particular formulation and conditions with AEROSIL® 150. The transparency of the silicone compound and the resultant vulcanized products rises significantly with the silica's BET surface.

Figure 4 Flow-curves of RTV-silicone of the BET-surface area.



If the mechanical properties of vulcanized sealants are examined in **Table 6**, the differences are less obvious than with compounds that have not been cross-linked. An increase in tensile strength and tear resistance can also be observed as the BET surface rises. The samples' elongation at break, Shore A hardness and resilience are only marginally affected in the chosen formulation.

Table 6 Mechanical properties of vulcanized sealant products as a function of the BET-surface of AEROSIL® fumed silica

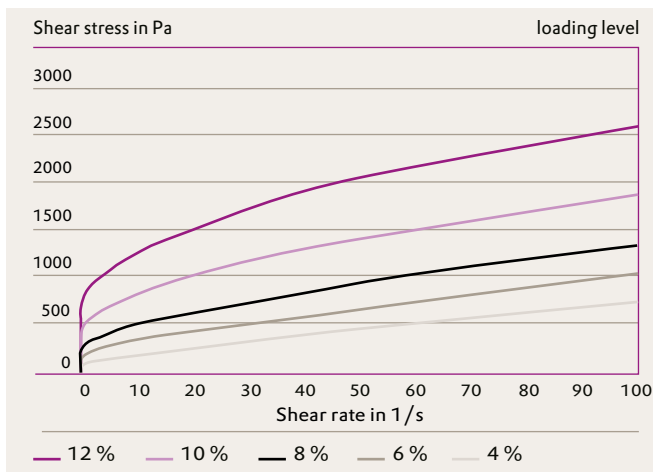
AEROSIL® fumed silica	90	130	150	200
Tensile strength [N/mm ²]	0.90	1.10	1.20	1.25
Elongation at break [%]	550	540	510	530
Tear resistance [N/mm]	1.9	2.5	2.6	2.9
Hardness, Shore A	12	15	15	14
Resilience [%]	40	43	46	42

5.1.2 Influence of the AEROSIL® Fumed Silica Concentration

Another possible way to influence the properties of 1 C silicone sealants is to vary the AEROSIL® concentration. In **Table 7**, the first properties described are those of silicone compounds which have not been cross-linked, based on the example of AEROSIL® R 972 when its concentration increased from 4% to 12%.

As the AEROSIL® concentration rises, the silicone compounds' viscosity and flow limit increase considerably. This is also evident from the flow curve pattern in **Figure 5**. Extrudability decreases accordingly. However, a sealant capable of being processed satisfactorily can also be produced using AEROSIL® R 972 at higher filling ratios. As the silica content rises, the surface of the silicone compound (assessed as the dispersion quality) appears somewhat uneven in the formulation and method used. At the same time, the transparency of the silicone compound and the resultant vulcanized products also decreases as the filling ratio rises. If the mechanical properties of vulcanized sealants are examined in **Table 8**, the reinforcing effect of AEROSIL® fumed silica increases with increasing concentration. As the AEROSIL® concentration rises, it is possible to observe a

Figure 5 Flow-curves of RTV-silicone sealants with AEROSIL® R 972 as a function of the loading level.



considerable improvement in tensile strength and tear resistance and an increase in Shore A hardness. Elongation at break and resilience are not affected significantly.

Table 7 Properties of non-cross-linked silicone sealant as a function of the AEROSIL® concentration.

AEROSIL® R 972	4%	6%	8%	10%	12%
Extrudability [g/min]	61.0	45.5	30.5	24	17.5
Viscosity [Pa s] at 10s ⁻¹	80	110	145	195	270
Flow limit [Pa]	55	122	190	365	545
Dispersion quality [Note]	1.0	1.5	1.5	2.0	2.5
Transparency [ΔE]	27.6	22.8	19.5	15.9	15.1

Table 8 Mechanical properties of vulcanized sealant products as a function of the AEROSIL® concentration.

AEROSIL® R 972	4%	6%	8%	10%	12%
Tensile strength [N/mm ²]	0.6	0.7	1.1	1.4	1.9
Elongation at break [%]	360	400	510	480	430
Tear resistance [N/mm]	1.3	1.8	2.5	3.4	4.2
Hardness, Shore A	8	10	13	17	23
Resilience [%]	56	53	44	51	50

5.1.3 Influence of the Hydrophobicity of AEROSIL® Fumed Silica

In contrast with the previous test series, both the specific surface and the silica concentration (8%) are kept constant in this series of experiments, so that the hydrophobic effect on the properties of 1 C silicone sealants can be observed. AEROSIL® 130 was chosen as an initial hydrophilic silica and compared with the hydrophobic silica AEROSIL® R 972 (AEROSIL® 130 after-treated using di-methyldichlorosilane or DDS). The experimental product* VP R 810 S was also tested as a very hydrophobic product with a comparable specific surface area.

This silica is aftertreated or rendered hydrophobic by means of hexamethyl disilazane or HMDS and exhibits tri-methylsilyl groups on the surface.

Chemically bonded carbon, which amounts to some 0.5% in AEROSIL® R 972 and some 2.0% in VP R 810 S, can be used as a gauge to measure hydrophobicity. As an initial test result, Table 9 indicates the properties of silicone compounds which have not been cross-linked.

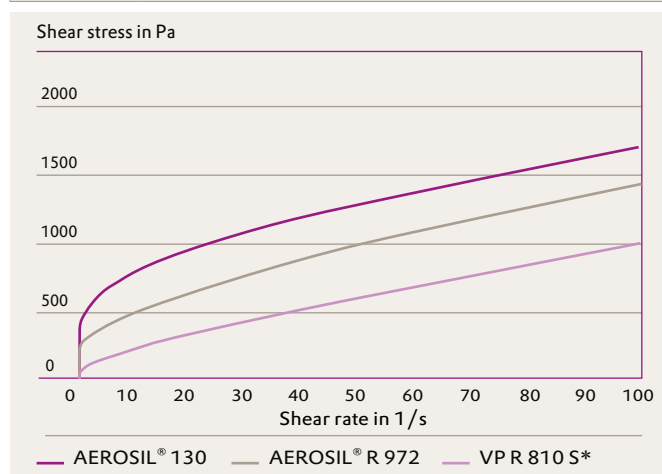
Table 9 Properties of non-cross-linked silicone sealant as a function of the hydrophobicity of AEROSIL® fumed silica

AEROSIL® fumed silica	130	R 972	VP R 810 S*
Extrudability [g/min]	27.5	30.5	38.5
Viscosity [Pa·s] at 10s ⁻¹	165	145	100
Flow limit [Pa]	370	190	50
Dispersion quality [Note]	2.5	1.5	1.5
Transparency [ΔE]	18.9	19.5	21.9

* Experimental product The physical and chemical properties are available on request.

As hydrophobicity rises, the thickening effect of AEROSIL® fumed silica drops, leading to greater extrudability of the silicone compounds and a reduced viscosity and flow limit. The flow curve pattern in Figure 6 highlights this feature. The influence of hydrophobicity on flow characteristics depends to a great extent on the type of cross-linking agent used (see section 5.1.6). The dispersion quality of silica is enhanced by the hydrophobic character. The transparency of the silicone compound and of the resultant vulcanized products increases marginally as hydrophobicity rises.

Figure 6 Flow-curves of RTV-silicone sealants as a function of the hydrophobicity of AEROSIL® fumed silica



The mechanical properties of vulcanized sealants in Table 10 exhibit only minimum hydrophobic effects.

The mechanical strength of vulcanized products, compared with the samples' tensile strength, tear resistance and elongation at break, do not suggest any effect caused by after-treated (hydrophobic) silicas. Only the samples' Shore A hardness drops slightly as the filler's hydrophobicity increases.

In the first two test series (influence of BET surface and the silica concentration) it was apparent that thickening of the non-crosslinked sealant is increased at the same time as the mechanical properties are improved. Consequently certain limits are imposed on the feasible mechanical characteristics of silicone compounds. As indicated by the last test series, these limits can however be slightly extended by after-treating the silicas.

Table 10 Mechanical properties of vulcanized sealant products as a function of the hydrophobicity of AEROSIL® fumed silica

AEROSIL® fumed silica	130	R 972	VP R 810 S*
Tensile strength [N/mm ²]	1.1	1.1	1.0
Elongation at break [%]	540	510	520
Tear resistance [N/mm]	2.5	2.5	2.3
Hardness, Shore A	15	13	12
Resilience [%]	43	44	48

5.1.4 Shelf Life of Silicone Sealants

1 C silicone sealants cannot be stored for unlimited periods. In addition to other constituents in the formulation, the pyrogenic silica affects the shelf life. To illustrate this effect, the two most common AEROSIL® types – hydrophilic AEROSIL® 150 and hydrophobic AEROSIL® R 972 – for silicone sealants were used in the formulation described in section 5.1.

Table 11 describes the changes in properties following warm storage (to simulate long-term storage of non-cross-linked silicone compounds at 80°C).

In the case of silicone compounds which contain a hydrophilic silica such as AEROSIL® 150 as an active filler, properties such as the viscosity or Shore A hardness and resilience of vulcanized products alter dramatically in some cases.

Table 11 Changes in properties after storage of the non-cross-linked silicone compound at 80°C.

	before	1 day	3 days	7 days	14 days
AEROSIL® R 972					
Viscosity [Pa·s] at 10s ⁻¹	153	154	150	152	-
Hardness, Shore-A	17	17	14	12	10
Resilience [%]	54	51	51	47	41
AEROSIL® 150					
Viscosity [Pa·s] at 10s ⁻¹	189	177	156	127	-
Hardness, Shore-A	15	12	10	3	1
Resilience [%]	52	45	36	20	5

After just 7 days of heat storage, vulcanization of the sealant is no longer satisfactory. If, on the other hand, a hydrophobic silica such as AEROSIL® R 972 is used, a silicone compound with considerably improved storage stability is obtained. The viscosity of this silicone compound remains almost constant. The Shore A hardness and resilience of these vulcanized products do not alter significantly either. The cause of this behaviour appears to be the lower number of reactive silanol groups which AEROSIL® R 972 introduces into the system.

5.1.5 Which AEROSIL® Fumed Silica for which Properties?

AEROSIL® 150 and AEROSIL® R 972 are the most frequently used AEROSIL® types in RTV-1 silicone sealants. AEROSIL® 130 can also be used as an alternative to hydrophilic AEROSIL® 150. If it is desirable to enhance the transparency of colourless silicone compounds, AEROSIL® R 974 should be used to achieve this effect, or AEROSIL® R 812 if highly transparent formulations are required. For increased clarity, the properties of the respective silicone compounds are summarized again in Table 12.

5.1.6 Effect of Formula Constituents on the Properties of Silicone Sealants

In addition to silica, other formula constituents such as crosslinking agents and adhesion promoters may also influence the properties of silicone sealants. In the experimental formula described at 5.1, the acetate cross-linking agent and the adhesion promoter were replaced with equivalent amounts (identical number of reactive groups) of an oxime cross-linking agent (cross-linking agent BO, Bayer AG) and its matching adhesion promoter (VP AC 3023, Bayer AG). 0.3% catalyst was added.

If the amount of adhesion promoter containing amino groups of 0.7% used in this formulation would be limited to approx. 0.4%, there would be comparable rheological properties as in an acetoxy formulation. But in silicas with varying degrees of hydrophobicity, this formula reveals the following interesting properties (Table 13).

Table 12 Properties of a non-cross-linked and a crosslinked silicone sealant (acetate formulation).

AEROSIL® fumed silica	130	150	R 972	R 974	R 812
Extrudability [g/min]	27.5	25.8	30.3	23.5	22.8
Viscosity [Pa s] at 10s ⁻¹	167	190	143	193	175
Flow limit [Pa]	371	409	190	336	211
Dispersion quality [Note]	2.5	2.0	1.5	2.5	3.0
Transparency [AE]	18.9	21.7	19.5	26.1	28.1
Tensile strength [N/mm ²]	1.1	1.2	1.1	1.1	1.1
Elongation at break [%]	540	510	510	420	500
Tear resistance [N/mm]	2.5	2.6	2.5	2.6	2.1
Hardness, Shore-A	15	15	13	20	19
Resilience [%]	43	46	44	51	58

Table 13 Properties of a non-cross-linked silicone sealant and the mechanical properties of vulcanized products as a function of the hydrophobicity of various AEROSIL® types (oxime formulation).

AEROSIL® fumed silica	130	R 972	VP R 810 S *
Extrudability [g/min]	19.8	22.4	32.2
Viscosity [Pa s] at 10s ⁻¹	113	103	90
Flow limit [Pa]	5	14	68
Dispersion quality [Note]	2.0	1.5	1.5
Transparency [DE]	17.5	18.0	19.5
Tensile strength [N/mm ²]	1.2	1.0	1.0
Elongation at break [%]	450	330	360
Tear resistance [N/mm]	2.1	2.2	2.1
Hardness, Shore-A	18	18	20
Resilience [%]	50	50	44

* Experimental product

In principle, if a hydrophilic silica such as AEROSIL® 130 is used, a self-levelling silicone compound with a very low flow limit is obtained. As the silica's hydrophobicity increases, viscosity decreases and extrudability rises. As can be seen, the compound's flow limit does in fact increase here, which should be regarded as a special feature, contrasting with the formula based on the acetate cross-linking agent.

5.2 Polysulphide Sealants

5.2.1 Comparison of AEROSIL® Fumed Silica and Precipitated Silicas

Generally speaking, both AEROSIL® fumed silica and precipitated silicas can be used to improve the non-sag properties of polysulphide sealants. Compared with precipitated silicas, AEROSIL® fumed silica can generally be used in smaller quantities to obtain the thixotropy necessary for preventing the sealants from sagging on vertical surfaces. Mechanical properties can also be enhanced by using silicas, as is the case with silicone rubber.

It should be mentioned here that both the electrical and the mechanical properties of polysulphide sealants are improved by using carbon black, for instance 5-30% PRINTEX® 3.

5.2.2 Rheological Properties of AEROSIL® Fumed Silica and Precipitated Silicas

The test formula for 2-component polysulphide sealants (cf. 8.1.2) was deliberately kept simple in order to highlight the effect of silica in the polymer, thus making it possible to record the differences in thickening behaviour.

The proportion of silica in 100 parts of polysulphide polymer was calculated as a starting parameter for the tests in order to achieve the required sag behaviour of 0 to 0.5 mm maximum in accordance with ASTM-D-2207 (cf. section 7). In contrast to the conventional approach (comparing the viscosities and rheological properties in equal concentrations), this particular one is necessary whenever several silicas are to be tested which differ substantially in their thickening behaviour. In comparing viscosities, it is only possible to draw very limited conclusions about sag behaviour, as will be shown below.

Table 14 lists the necessary concentrations and parts of various AEROSIL® types compared with the various precipitated silicas. The differences between the individual AEROSIL® and precipitated silica types in terms of their thickening properties are quite evident. According to these tests, hydrophobic AEROSIL® R 202 is the most effective thickening silica in the LP 977 test polymer. If the thickening properties of hydrophilic AEROSIL® 200 are compared with hydrophobic AEROSIL® R 805, R 805 requires fewer parts to obtain the desired sag behaviour.

The fact that fairly high concentrations are needed to achieve the sag behaviour of 0-0.5 mm is true of all the precipitated silicas tested - with the exception of SIPERNAT® 383 DS and SIPERNAT® 500 LS. SIPERNAT® 383 DS and SIPERNAT® 500 LS are therefore inexpensive alternatives to the hydrophilic pyrogenic silicas. The hydrophobic precipitated silicas SIPERNAT® D 10 and D 17 should be used whenever the polysulphide sealants are to be filled as much as possible for certain applications. Consequently, in the case of LP 977, which has a relatively low viscosity, as much as 22% of SIPERNAT® D 10 are required for a stable product.

Based on a few selected silicas, the following section discusses correlations between

- viscosity and sag behaviour,
- sag behaviour and flow limit and
- viscosity and extrudability in polysulphide sealants.

Table 14 List of all tested silicas related to 100 parts polysulphide polymer.

AEROSIL® R 202	5 parts	SIPERNAT® 500 LS	11.5 parts
AEROSIL® R 805	7 parts	SIPERNAT® 383 DS	13 parts
AEROSIL® R 812 S	9 parts	SIPERNAT® 320 DS	15 parts
AEROSIL® R 812	10 parts	SIPERNAT® D 10	27.5 parts
AEROSIL® R 972	14 parts	SIPERNAT® D 17	20 parts
AEROSIL® R 974	13 parts		
AEROSIL® 200	12 parts		

Viscosity and Sag Behaviour

Figure 7 shows that there is no correlation between viscosity and sag behaviour, i.e. the sealant can still sag even with a very high viscosity. This also applies to high filler additives based on natural products, which can be used to obtain high viscosities but not thixotropic properties.

Flow Limit and Sag Behaviour

Figure 8 compares the flow limits of different samples from Table 15 with sag behaviour measurement values. The flow limits were ascertained here by means of a cone-and-plate rheometer based on Casson's regression model. It can be seen that the flow limit correlates well with the sag behaviour. It is therefore possible to use the flow limit to quantify sag behaviour.

Figure 7 Correlation viscosity versus sag behaviour.

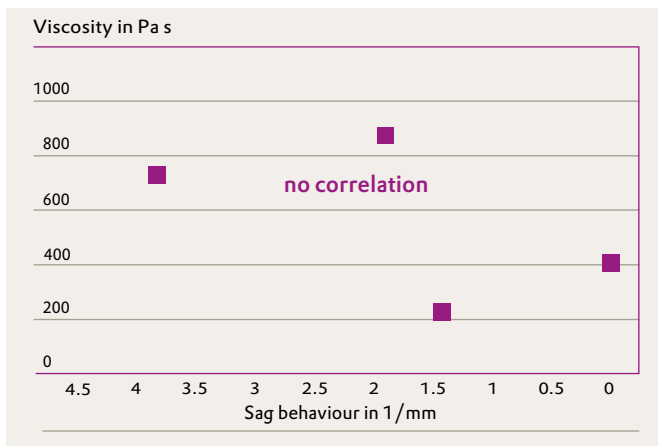
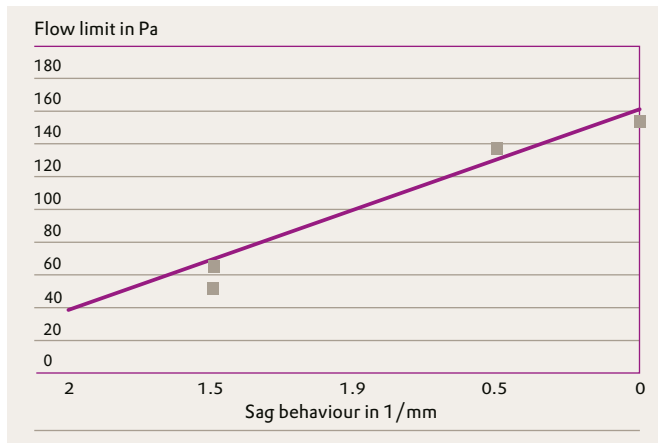


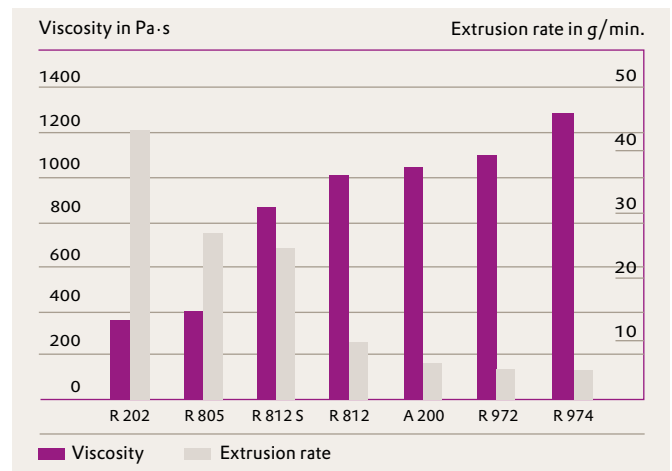
Figure 8 Correlation flow limit versus sag behaviour.



Viscosity and Extrudability

Figure 9 shows that there are significant correlations between viscosities and extrudability rates. The higher the compound's viscosity, the lower the extrudability.

Figure 9 Viscosity and extrudability.



5.2.3 Storage Stability

Storage stability is generally defined as the ability to maintain constant rheological properties in the sealant throughout a specific period, i.e. the sealant's viscosity or extrudability do not increase or decrease substantially during storage. Constant rheological properties over several months are very important, as otherwise it is no longer possible to process sealants satisfactorily. Table 15 shows the measured viscosities, extrudabilities and the sag behaviours of the polysulphide sealants thixed with AEROSIL® fumed silica and precipitated silicas after being stored at room temperature for 16 weeks.

With regard to the sag behaviour, all thixed polysulphide sealants show good to excellent storage stabilities with exception of the thixed sealants using AEROSIL® 200, AEROSIL® R 972 and AEROSIL® R 974. Especially in the case of the thixed sealants using SIPERNAT® D 10 and SIPERNAT® 383 DS the adjusted sag behaviour remained constant even after being stored for 16 weeks.

Table 15 Storage stability of polysulphide sealants thixed with various silicas.

Silica		Viscosity in Pa s (5 rpm)		Extrudability in g/min		Sag behaviour in mm	
		parts	1 day	16 weeks	1 day	16 weeks	1 day
without	-	8	1	100	-	down	down
AEROSIL® R 202	5	419	392	55	46	0	1.0
AEROSIL® R 805	7	474	424	32	29	0.5	1.5
AEROSIL® R 812 S	9	922	831	28	22	0	1.0
AEROSIL® R 812	10	1088	945	10	12	0.5	1.0
AEROSIL® R 972	14	1082	915	7	7	3.0	4.5
AEROSIL® R 974	13	1306	1120	6	7	1.5	4.0
AEROSIL® 200	12	953	812	6	4	0.5	4.0
SIPERNAT® D 10	27.5	800	880	4	6	0	0
SIPERNAT® D 17	20	819	864	9	10	0	1
SIPERNAT® 320 DS	15	1024	910	12	12	0	1
SIPERNAT® 383 DS	13	1306	1290	14	14	0	0
SIPERNAT® 500 LS	11.5	998	815	12	11	0	1

5.2.4 Reinforcing Properties of AEROSIL® Fumed Silica and Precipitated Silicas

Even if the function of AEROSIL® fumed silica and precipitated silicas is most significant in silicone compounds, considerable improvements in the mechanical properties were found in other sealants. **Table 16** indicates the mechanical properties of various AEROSIL® types and precipitated silicas in polysulphide sealants tested in the previous section. A point of interest is that on the

basis of all silicas tested with different loadings, mechanical properties of relatively even quality are obtained in the short-chain test polymer LP 977. As the proportion of filler rises, higher tear resistance achieved.

Table 17 shows another example of how to improve the mechanical properties of a 1 K polysulphide sealant filled with chalk by adding AEROSIL® fumed silica.

Table 16 Mechanical properties of polysulphide sealants with various silicas.

Silica	parts	Tear strength [N/mm]	Resilience [%]	Shore-A- Hardness
AEROSIL® R 202	5	3.4	54	49
AEROSIL® R 805	7	3.9	52	51
AEROSIL® R 812 S	9	4.7	46	47
AEROSIL® R 812	10	4	50	51
AEROSIL® R 972	14	5.9	48	55
AEROSIL® R 974	13	5.6	48	51
AEROSIL® 200	12	6.6	49	55
SIPERNAT® D 10	27.5	8.1	40	61
SIPERNAT® D 17	20	6.1	40	48
SIPERNAT® 320 DS	15	5.0	44	51
SIPERNAT® 383 DS	13	5.0	47	54
SIPERNAT® 500 LS	11.5	4.4	45	48

Table 17 Improving mechanical properties of a vulcanised 1- component polysulphide sealant with different calcium carbonate fillers by adding AEROSIL® fumed silica (test formula 8.1.3).

Formulation	Modulus 100 [%]	Tensile strength [N/mm ²]	Elongation at break [%]	Tear resistance [N/mm]	Shore-A- Hardness	
1) Winnofil S	15	0.3	1.1	1000	4.3	15
AEROSIL® 130	-					
2) Winnofil S	15	0.4	1.6	1000	5.6	21
AEROSIL® 130	1.5					
3) Omya BSH	15	0.2	0.7	900	3.6	13
AEROSIL® 130	-					
4) Omya BSH	15	0.4	1.4	900	5.5	23
AEROSIL® 130	1.5					

5.3 Polyurethane Sealants

5.3.1 Particularly Suitable Silicas

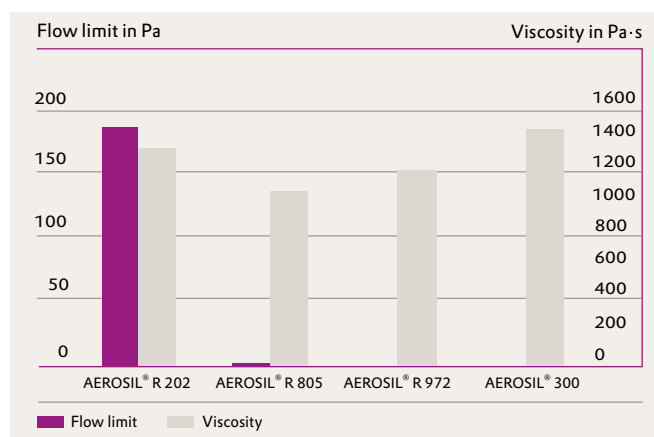
In terms of storage stability and rheological properties, hydrophobic AEROSIL® types – particularly AEROSIL® R 202 – enjoy the following benefits over hydrophilic AEROSIL® fumed silica and precipitated silicas for PUR sealants:

- Due to the higher water absorption rate of hydrophilic AEROSIL® types, the prepolymers' isocyanate groups react with water to form urethane groups and CO₂. These side reactions may take place very quickly, depending on the concentration of water and isocyanate. Examples are a viscosity increase of the sealant or partial hardening of the compounds in the cartridge.
- Due to the hydrophobic surface groups, the water absorption rate of hydrophobic AEROSIL® types R 202 and R 972 are much lower (cf. Figure 1), making it generally impossible for these side reactions to occur. These statements primarily apply to 1-component PUR sealants. As far as 2-component PUR sealants are concerned, hydrophilic AEROSIL® types – particularly AEROSIL® 150 – can also be used to render the polyol component thixotropic, since generally there are no such side reactions between the polyol component and the adsorbed water (cf. guide formula 8.2.3).
- Precipitated silicas cannot be used as thickeners for polyurethane sealants because the water content of approx. 3-6% is too high. The stoichiometric characteristics are altered by the reaction of isocyanate with water, which causes incomplete hardening of the sealant.
- Unlike the other AEROSIL® types and precipitated silicas, AEROSIL® R 202 can be used to obtain a defined flow limit, which is crucial for non-sag properties.

5.3.2 Rheological Properties of Hydrophilic and Hydrophobic AEROSIL® Types

Figure 10 compares the rheological efficiencies of the hydrophobic silicas AEROSIL® R 202, R 805 and R 972 with the hydrophilic silica AEROSIL® 300 in Desmodur E 25, a base material for 1-component PUR sealants. It can be clearly seen that a high flow limit is achieved in this system only by using AEROSIL® R 202. Although other AEROSIL® types can be used to achieve high viscosities, the flow limits measured are low. In other words, the sealant beads would exude from the joints when applied.

Figure 10 Flow limit and viscosity of Desmodur E 25 thixed with 10% various AEROSIL® types.



AEROSIL® R 202 also has advantages over AEROSIL® R 805, R 972 and AEROSIL® 150 in storage stability tests (Figure 11 and 12). The sealant system thixed with AEROSIL® 150 has completely hardened after a only one month storage. The flow limits and viscosities of the system rendered thixotropic with AEROSIL® R 202 increase only very slightly. AEROSIL® R 202 exhibits the most favourable characteristics in the test carried out here.

Figure 11 Flow limits of 1 C-polyurethane sealants thixed with various AEROSIL® types after incorp. and 1 month.

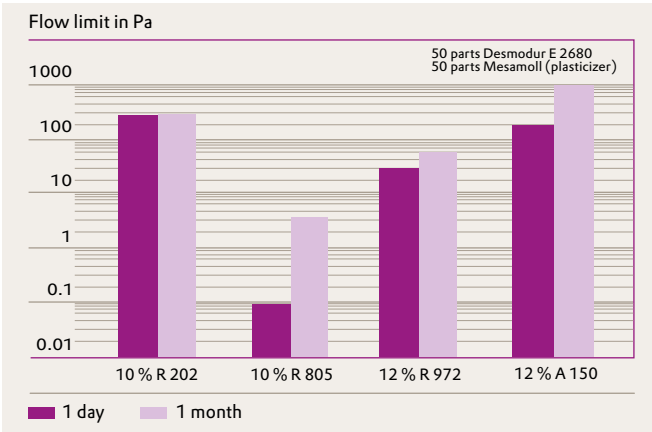
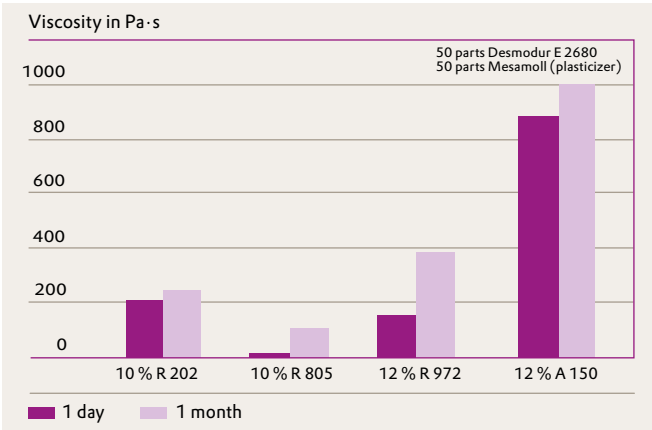


Figure 12 Viscosities ($10s^{-1}$) of 1 C-polyurethane sealants thixed with various AEROSIL® types after incorp. and 1 month.



5.4 Polyvinyl Chloride Sealants

5.4.1 Significance of AEROSIL® Fumed Silica

AEROSIL® 200, AEROSIL® 300 and AEROSIL® 380 are also used as additives to regulate viscosity in the field of PVC plastisols. The effect achieved with AEROSIL® fumed silica relates to the increase in viscosity usually associated with distinct thixotropy and pseudoplasticity and the ability to obtain a defined flow limit. Sealants with a paste-like consistency can be easily delivered and processed as a result of this marked pseudoplasticity, yet the high thixotropy and flow limit mean that after being applied these substances remain in position as thick sealant beads without spreading.

5.4.2 Influence of the BET Surface

The effect of the BET surface of AEROSIL® 200, 300 and 380 on the stability of PVC plastisols is illustrated by the following test formula (cf. 8.1.5). The flow limit was used as a measurement value. **Figure 13** clearly shows that the flow limit increases with the specific surface. As already discussed in section 5.2.2, there is good correlation between the flow limit and stability and/or sag behaviour.

5.4.3 Storage Stability

In **Figure 14**, the flow limits of PVC plastisols are shown directly after their production and after having been stored for 1 and 3 months respectively. How the different dispersion equipments e.g. triple roll mill, planetary dissolver and kneader, affect the storage stability of PVC plastisols can clearly be seen. The best dispersion of AEROSIL® fumed silica in PVC plastisol is achieved using the triple roll mill. There is no drop in the flow limit after 3 months. The greatest drop in flow limits after 3 months can be seen when dispersion is carried out with the kneader, indicating that the dispersion of AEROSIL® fumed silica had not reached its optimum extent and that the incorporation method, e.g. based on a batch process needs to be optimized.

5.5 Polyacrylate Sealants

Table 18 shows the advantage of AEROSIL® 200 in an acrylic resin sealant at a fairly high temperature. Without substantially altering extrudability, mixtures containing AEROSIL® fumed silica reveal excellent non-sag properties, which is manifested in a fairly small run distance.

Figure 13 Flow limits of PVC plastisols as a function of BET-surface area.

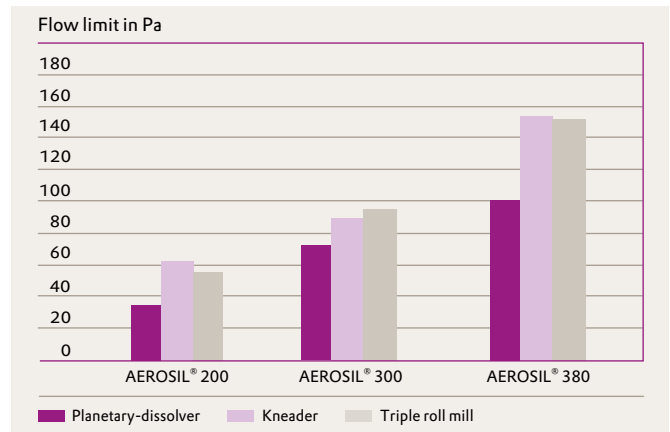


Figure 14 Flow limits of PVC plastisols as a function of incorporation method after 1 day, 1 month and 3 months.

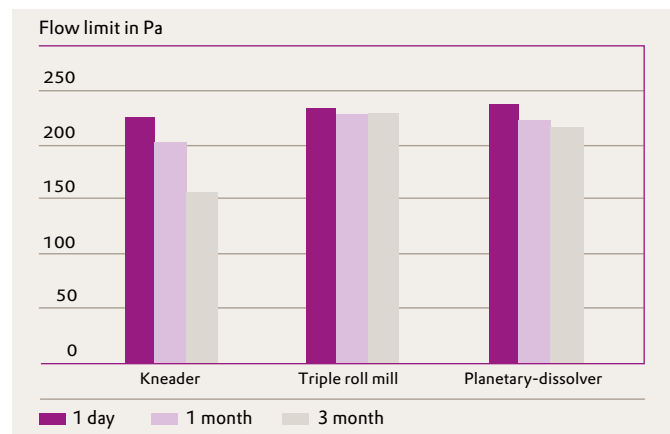


Table 18 Effect of AEROSIL® 200 in an acrylic joint sealing compound at 50 °C (test formulation 8.1.6).
¹⁾ at room temperature
²⁾ in accordance with Canadian Specification Board 19-GP-5

Formulation	Storage time [days] ¹⁾	Extrusion properties ²⁾ [g/min]	Run-off distance ²⁾ [mm]
without AEROSIL® fumed silica	1	250	100 (compl. run-down)
	28	230	100 (compl. run-down)
1.1 % AEROSIL® 200	56	240	100 (compl. run-down)
	1	170	5
	28	180	10
2.2 % AEROSIL® 200	56	170	10
	1	130	0
	28	140	0

6 General Aspects of the Dispersibility of Silicas

In ensuring the optimum efficacy of synthetic silicas in sealants, an important factor is the presence of a high degree of dispersion in the form of „aggregates“ which generally cannot be further disintegrated by the influence of even higher shearing forces. The filler aggregates should also be distributed as homogeneously as possible within the polymer. Ideally, the best reinforcing properties and thickening effects can be achieved by high-surface AEROSIL® types, i.e. pyrogenic silicas based on small primary particles. It has however been found in practice that synthetic silicas are harder to disperse as the BET surface increases. It has also been noticed that hydrophobic silicas are easier to disperse than the corresponding initial hydrophilic silicas. This is due to the lower silanol group concentration in hydrophobic products which results in fewer of hydrogen cross links between the silica particles. This is substantiated by observation of particularly large aggregates in electron microscope tests on precipitated silicas in which the production process causes the silanol group concentration to be some three times greater than in comparable AEROSIL® types. In the case of precipitated silicas manufactured by Evonik, the mean agglomerate size rather than the mean primary particle size is therefore quoted in the relevant literature.

The tapped density is another property of powder-form silica that is significant in terms of the dispersibility of silicas in polymers. As tapped density rises, higher shear forces are necessary for optimum dispersion. Due to practical considerations regarding the economical production of sealants (storage, reduction of incorporation time) and for reasons of commercial hygiene (dust formation), it is frequently desirable to use AEROSIL® types with a higher tapped density than the conventional 50 g/l. The following test results (cf. Tables 19 and 20) are based on a 1 C silicone sealant and indicate that higher tapped densities can be used. The dispersion equipment determines what tapped density can be used. The AEROSIL® types described here were densified by means of a completely new process that enables tapped densities of up to 150 g/l to be achieved. More detailed information on densified AEROSIL® types is available on request. These products are designated „VV“ to differentiate them from the conventional versions.

Table 19 Properties of uncured 1 C -RTV silicone sealants.

Silica 8 %	Incorporation time [min]	Extrudability [g/min]	Anti sag [grade]	Dispersion quality [grade]	Transparency [grade]
AEROSIL® 150 standard	1.7	17.9	1.0	2.5	2.0
AEROSIL® 150 silo/undensified	2.0	19.3	1.0	3.5	2.0
AEROSIL® 150 VV 50	1.5	21.6	1.0	2.5	2.0
AEROSIL® 150 VV 75	1.0	22.2	1.0	2.0	2.0
AEROSIL® 150 VV 100	1.0	25.5	1.5	3.0	2.0

Table 20 Properties of cured 1 C -RTV silicone sealants.

Silica 8 %	Tensile strength [N/mm ²]	Elongation [%]	Tear resistance [N/mm]	Shore-A-Hardness	Impact resilience [%]
AEROSIL® 150 standard	1.2	400	2.4	16	55
AEROSIL® 150 silo/undensified	1.3	450	2.4	16	51
AEROSIL® 150 VV 50	1.4	450	2.3	17	54
AEROSIL® 150 VV 75	1.4	440	2.4	17	56
AEROSIL® 150 VV 100	1.4	430	2.2	17	53

7 Description of Certain Specific Test Methods

Equipment such as planetary mixers, planetary dissolvers, dissolvers and extruders, is used to disperse AEROSIL® fumed silica in sealants. The planetary dissolver (a laboratory version is shown in Figure 15) in particular has proved highly effective for producing paste-like sealants, since it combines the advantages of thorough blending (planetary arms) with excellent dispersion (dissolver disk). Particularly high shear forces are achieved close to the serrated disk edge between the fast-moving dissolver disk and the slower moving sealant (14). The silica agglomerates can therefore be easily converted into silica aggregates. The guide values for peripheral speeds and geometric dimensions quoted in Figure 18 apply to dissolvers in general (15).

tip speed m/s: 8-20

Diameter stirring blade/diameter dispersion container = 0.2–0.5

Distance from bottom

stirring blade/diameter dispersion container = 0.3–0.5

Filling level (height)/diameter dispersion container = 1

Figure 15 Lab planetary dissolver with vacuum- and inert gas equipment (Hermann Linden GmbH & Co., KG, D-51709, Marienheide, Germany).



7.1 Extrudability

In accordance with Canadian standard CGSB 19-GP-5, a putty gun with an air pressure of about 0.6 N/mm² is used to press the sealant contained in a cartridge through a circular nozzle of approx. 6 mm diameter into a calibrated vessel. The quantity in weight per time unit is determined.

In accordance with ASTM D 2452-69 T and similar to the above specification, the weight per time unit expelled by air pressure is calculated on the basis of a standardized nozzle with a pressure of approx. 0.2 N/mm². Measurements can also take account of the temperature.

7.2 Sag Behavior

In accordance with ASTM D 2202-88, the sealant is filled into a standardized test block and stored in an upright position at room temperature. The run distance of the filled sealant's lower edge is measured in millimetres.

In accordance with Canadian standard CGSB 19-GP-5, the sealant is filled into a standardized test channel (length 25.4 cm, of which 12.2 cm filled with sealing compound. Width 1.92 cm, depth 1.27 cm) and stored in an upright position for one hour at 50 °C. The run distance of the filled sealant's lower edge is measured in millimetres: 100 mm means that the compound has been completely expelled.

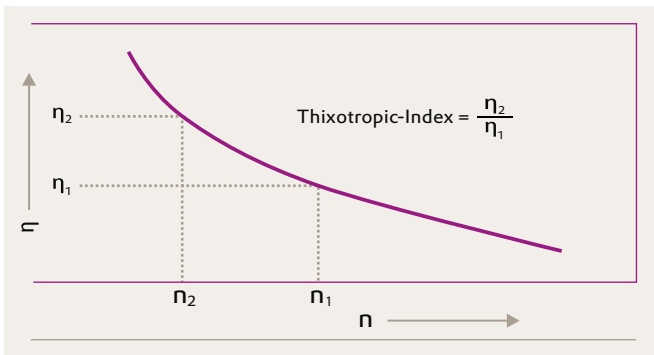
7.3 Measuring Thixotropy

If AEROSIL® fumed silica is dispersed in a liquid resin, the surface silanol groups interact either directly or indirectly via the polymer molecules. This affinity is due to hydrogen cross links and results in a temporary three-dimensional structure that becomes macroscopically „visible“ as thickening. When subjected to mechanical load, such as intensive stirring or agitation, this network disintegrates. The system has a low viscosity. In its neutral state, the AEROSIL® particles reassociate and the viscosity regains its original value.

An absolute gauge for thixotropy cannot be obtained by normal viscosity measurements. The following three test methods usually suffice in ascertaining and comparing the thixotropic value in approximate terms:

1. Thixotropic index (cf. Figure 16)
2. Thixotropic area
3. Viscosity/time curves

Figure 16 Explanation of the Thixotropic Index.



7.3.1 Thixotropic Index

The thixotropic index is defined as the quotient of two viscosities calculated at different speeds. In practice this index is ascertained using a rotational viscosimeter. The speeds n_1 and n_2 usually have the ratio of 1 : 10.

In other words, the test is basically a gauge for the steepness of the viscosity curves and hence for the pseudoplasticity. But since thixotropic systems always exhibit a pseudoplastic behaviour, sealants with a thixotropic index of >3 can be considered as sufficiently thixotropic.

7.3.2 Thixotropic Area

The thixotropic area is defined as the hysteresis area between the upward and downward curves on a recorded flow curve. It is assumed that the larger this area is, the greater the thixotropy in general. This method does however entail practical disadvantages in terms of the extent to which results can be reproduced and qualified accurately.

7.3.3 Viscosity/Time Graphs

In viscosity/time graphs, the substance's viscosity is reduced to a minimum by means of a rotational rheometer with a constant shear. Reformation is then measured either at a very low shear rate or non-destructively by means of oscillation. The more effectively and quickly the original viscosity rebounds, the greater the thixotropy.

8 Testing Formulations

8.1 Testing Formulations

Test formula 8.1.1 (see section 5.1)

1C silicone sealant

		% by weight
Silicone polymer		
Silopren E 50	(8.3.1)	62.4
Silicone oil M 1000	(8.3.1)	24.6
Ethyltriacetoxysilan		4.0
Dynasylan® BDAC		1.0
Catalyst (dibutyl tin diacetate)		0.01
AEROSIL® R 972	(8.3.2)	8.0
		<u>100.0</u>

Test formula 8.1.2 (see section 5.2)

2C polysulphide sealant

		% by weight
Component A		
Thiokol LP 977	(8.3.3)	95.2
AEROSIL® R 202	(8.3.2)	4.8
		<u>100.0</u>
Component B		
Manganese dioxide	(8.3.4)	50.0
Plasticizer (dibutyl phthalate)		50.0
Catalyst (dibutyl tin diacetate)		0.01
		<u>100.0</u>
Mixture ratio:		
100 parts by weight	Component A	
40 parts by weight	Component B	

Test formula 8.1.3 (see section 5.2.4)

1C polysulphide sealant

		% by weight
Thiokol LP 32	(8.3.3)	37.5
Plasticizer		19.3
Adhesive resin		3.7
Chalk		15.0
Kaolin		5.1
Rutile titanium dioxide	(8.3.13)	11.2
AEROSIL® 130	(8.3.2)	1.5
Na perborate paste		6.7
		<u>100.0</u>

Test formula 8.1.4 (see section 5.3)

1C polyurethane sealant

		% by weight
Desmodur E 25	(8.3.1)	45.5
Plasticizer (e.g. Mesamoll)	(8.3.1)	45.5
AEROSIL® R 202	(8.3.2)	9.0
		<u>100.0</u>

Test formula 8.1.5 (see section 5.4)

PVC plastisol underseal compound

		% by weight
E-PVC		15.6
Chalk		38.9
Calcium oxide		1.6
AEROSIL® 380	(8.3.2)	0.9
Stabilizer		0.5
Adhesion agent (e.g. Dynasylan® MTMO)		1.0
Plasticizer (e.g. dioctyl phthalate)		40.4
Thinner		1.1
		<u>100.0</u>

Test formula 8.1.6 (see section 5.5)

Polyacrylate sealant

		% by weight
Polyacrylate sealant	(8.3.6)	44.7
Pine Oil		0.5
Ethylene glycol		0.7
Dibutylsebacate		0.7
Chalk		43.4
Talcum		7.8
AEROSIL® 200	(8.3.2)	2.2
		<u>100.0</u>

8.2 Guide Formulation

Guide formation 8.2.1

2C polysulphide sealant

		% by weight
Component A		
Thiokol LP 32	(8.3.3)	47.8
Plasticizer		16.6
Chalk		12.5
Kaolin		14.8
Rutile titanium dioxide	(8.3.13)	4.8
Adhesive resin		1.0
Dynasylan® GLYMO	(8.3.2)	1.5
AEROSIL® R 202	(8.3.2)	1.0
		<u>100.0</u>
Component B		
Manganese dioxide	(8.3.4)	50.0
Plasticizer		46.0
Accelerator		4.0
		<u>100.0</u>

Guide formation 8.2.2 1 C polysulphide sealant

		% by weight
Thiokol LP 32	(8.3.3)	34.0
Plasticizer		14.0
Fillers		36.5
Adhesive resin		3.0
BaO (drying agent)		2.0
Calcium peroxide*		5.0
Plasticizer*		3.0
AEROSIL® R 202	(8.3.2)	2.5
		<u>100.0</u>

* rubbed together and added as a paste

Guide formation 8.2.3 2C polyurethane sealant, stable under load and flexible for expansion joints in construction engineering according to (13)

Component A

Desmophen 250 U	(8.3.1)	1.1
Plasticizer, e. g. Mesamoll	(8.3.1)	19.6
Vulkanox BKF	(8.3.7)	0.4
Calcium octoate, 4 % Ca	(8.3.8)	0.5
Ceasit I calcium stearate	(8.3.9)	3.3
AEROSIL® 150	(8.3.2)	2.0
Millicarb	(8.3.11)	45.0
Bayer titanium R-KB-4	(8.3.13)	4.5
Catalyst mixture		0.5

Component B

Desmodur E14	(8.3.1)	18.5
Plastic black paste	(8.3.2)	0.2
Plasticizer, e. g. Mesamoll	(8.3.1)	2.4
AEROSIL® R 202	(8.3.2)	2.0
		<u>100.0</u>

Catalyst mixture

Coscoat 83	(8.3.11)	50.0
Dibutyltin dilaurate		5.0
Plasticizer, e.g. Mesamoll	(8.3.1)	45.0
		<u>100.0</u>

Mixture ratio:

100 parts by weight	Component A
30-35 parts by weight	Component B

Processing time: approx. 2 hours

Guide formulation 8.2.4 1 C polyurethane sealant for constructional seals in accordance with (13)

Stage 1

		Grey-Parts by weight	Black-Parts by weight
Additive VP LS 2996 E (special plasticizer)	(8.3.1)	21.0	21.0
Desmodur E 2680 (MDI prepolymer)	(8.3.1)	10.0	10.0
Solvic 373 MC	(8.3.5)	20.0	20.0
Omya filler BLP-3	(8.3.10)	14.8	18.5
Bayer titanium R-FK-2		4.0	-
AEROSIL® R 202	(8.3.2)	2.0	2.0
Plastic black paste	(8.3.2)	0.2	-
Carbon black PRINTEX® 60	(8.3.2)	-	0.5

Stage 2

Additive VP LS 2996 E	(8.3.1)	2.1	2.1
Desmodur VH 20	(8.3.1)	0.5	0.5

Stage 3

Desmodur E 2680	(8.3.1)	10.0	10.0
-----------------	---------	------	------

Stage 4*

Dynasylan® GLYMO	(8.3.2)	0.3	0.3
Additive T1		0.4	0.4
Xylol / Exxsol 030 2:1		2.3	2.3
DBTL, 10 %		0.4	0.4

Stage 5

Desmodur E 2680	(8.3.1)	12.0	12.0
		<u>100.0</u>	<u>100.0</u>

* premix; prepare at least 24 h before processing

Guide formulation 8.2.5 Polyacrylate dispersion sealant containing no plasticizers, for interior joints in accordance to (19)

		% by weight
Acronal V 271 pH 8	(8.3.12)	35.0
Lumiten N-OG		0.2
Pigment distributor N		0.1
Omya BLP3	(8.3.10)	33.3
Calcidar 5	(8.3.10)	31.0
AEROSIL® R 974	(8.3.2)	0.4
		<u>100.0</u>

Guide formulation 8.2.6

Polyacrylate sealant, translucent

		% by weight
Rheoplex E-2620	(8.3.6)	82.33
Sodiumlauryl sulphate		0.13
Water		1.13
Kathon LX 1.5 %	(8.3.6)	0.06
Propylene glycol		0.85
Ethylene glycol		0.85
Mineral oil		5.65
Adhesion agent		0.46
Ammonium hydroxide (28 % NH ₃)		0.85
Water		4.83
Skane M-8	(8.3.6)	0.06
AEROSIL® 200	(8.3.2)	2.80
		<u>100.00</u>

9 Product Safety Aspects for the Handling of Synthetic Silicas

8.3 List of Suppliers

- 8.3.1 GE Bayer Silicones
D-51368 Leverkusen
www.gebayersilicones.com
- 8.3.2 Evonik Industries AG, 63457 Hanau, Germany
www.evonik.com
- 8.3.3 Thiokol-Gesellschaft mbH,
D-68305 Mannheim-Waldhof
- 8.3.4 Honeywell Speciality Chemicals Seelze GmbH
D-30926 Seelze
www.honeywell.seelze
- 8.3.5 Deutsche Solvay-Werke GMBH, D-47495 Rheinberg
www.solvay.de
- 8.3.6 Rohm & Haas, Philadelphia, Penn., USA
www.rohm&haas.com
- 8.3.7 Rhein Chemie Rheinau GmbH
D-68219 Mannheim
www.rheinchemie.com
- 8.3.8 Borchers GmbH, D-40007 Düsseldorf
www.borchers.de
- 8.3.9 Chemische Werke München, O. Bärlöcher GmbH,
D-85761 Unterschleißheim
www.baerloecher-com.ae.psiweb.com
- 8.3.10 Omya GmbH, D-50968 Köln
www.omya.de
- 8.3.11 C. H. Erbslöh, D-47809 Krefeld
www.cherbsloeh.de
- 8.3.12 BASF AG, D-67056 Ludwigshafen
www.basf.de
- 8.3.13 Kronos Titan GmbH, D-51373 Leverkusen
www.kronos.de

All synthetic silicas supplied by Evonik are manufactured either by the precipitation method in an aqueous solution or by flame hydrolysis and are characterised by powder diffractometer pictures. The absence of sharp peaks reveals that the synthetically manufactured silicas have an entirely amorphous form.

When handling amorphous silica, intake by inhalation is of particular significance: if for instance the TLV of 4 mg/m³ is reached when handling amorphous precipitation silicas, no damage to the health has yet been observed. If the TLV is exceeded, it can constitute a mechanical burden to the upper respiratory tract in the same way as other dusts, and protracted exposure can then lead to functional and organic damage to the respiratory passages.

No signs of irritation have yet been observed following brief contact with the skin or mucous membranes. Neither have any sensitization symptoms been detected in persons who have worked with synthetic silicas over many years. However, the explicit property of adsorbing water and oil can lead to dry, scaly skin after protracted or repeated contact.

Regular medical checks carried out on workers who have been employed for many years at production plants for synthetic amorphous silicas have not detected a single case of silicosis (16–18). Experiments carried out on animals have largely confirmed the findings for humans on the handling of Evonik silicas. The one-off application of silicas to intact or scarified areas of skin on rats did not produce symptoms of irritation to the skin. As a general rule, no harmful effect was observed. Even the introduction of precipitated silicas into the tear sacs of rabbits did not cause any damage. The acute oral toxicity value, LD₅₀, for synthetic silicas is greater than 10.000 mg/kg for the tests carried out on rats.

The silicas referred to here are delivered in paper sacks. Transport by silo vehicle is also possible. Extensive handling tests have been carried out on synthetic silicas: in order to devise practical means of avoiding the formation of dust. The results of these tests are summarised in issue number 28 of the Evonik Technical Bulletin series. These results cover:

- manual or fully-automated debagging,
- internal transport by means of suction or pressure,
- automatic weighing and batching,
- dust-free adding to mixing and dispersion equipment.

According to the chemicals legislation of the European Union, amorphous synthetic silicas are not classified as hazardous substances. Not classified as hazardous goods for purposes of transport.

For further information on product safety please see the corresponding safety data sheets and issues 65 and 76 of the Technical Bulletin series.

10 References to Published Sources

- (1) H. FERCH, IX. Fatipec Congress proceedings, p. 144 (1968)
- (2) FERCH in: Chem. Ing. Tech. No. **48**, p. 922 (1976)
- (3) German Patent Document DE-PS 870242, Degussa (1941)
- (4) WAGNER, E. and H. BRUNNER in: Angew. Chem. No. **72**, 744 (1960)
- (5) „Desmodur/Desmophen, solventfree polyurethane basic materials for coatings and sealants“, company publication, Bayer AG, D-51368 Leverkusen (1988)
- (6) E.SCHINDEL-BIDINELLI:
„Strukturelles Kleben und Dichten“, publ. Hinterwaldner-Verlag, Munich, Germany (1988)
- (7) H. LUCKE in „Ullmanns Enzyklopadie der technischen Chemie“, Vol. 14, publ. VCH Verlagsgesellschaft, D-69469 Weinheim (1977)
- (8) R. HOUWINK, Kautschuk, Gummi, No. **5**, (5), WT 65 (1952)
- (9) M. L. STUDEBAKER in:
Rubber Chem. Technol. No. **30**, p. 1400 (1957)
- (10) E. M. DANNENBERG in: Rubber Chem. Technol. No. **48**, p. 410 (1957)
- (11) G. KRAUS in: Fortschr. Hochpolym. Forschung No. **8**, p. 155 (1971)
- (12) S. WOLFF, „Verstärkung von Elastomeren und Kunststoffen durch Füllstoffe“, GdCH-Seminar 620/90 (1990)
- (13) Guideline formulation from the Basic Paint Materials and Special Areas Division, Applications Technology, Bayer AG, D-51368 Leverkusen
- (14) M.ZLOKARNIK in „Ullmanns Enzyklopadie der technischen Chemie“ Vol. 14, publ. VCH Verlagsgesellschaft, D-69469 Weinheim (1977)
- (15) H.-P. WILKE: „Rührtechnik, verfahrenstechnische und apparative Grundlagen“, publ. Hüthig-Verlag, D-69018 Heidelberg
- (16) FERCH, H. and S. HABERSANG in:
Seifen, Ole, Fette, Wachse No. **108**, p. 487 (1982)
- (17) ISAAC, O. and H. FERCH in: Dtsch. Apoth. Z. No. **116**, p. 1867 (1976)
- (18) FERCH, H., GEROFKE, H., ITZEL, H. and H. KLEBE in:
Sozialmed. Präventivmed. Arbeitsmed. No. **22**, pp. 6 and 33 (1987)
- (19) Guideline formulation from the adhesive raw material division, BASF AG, D-67056 Ludwigshafen

11 Physical and Chemical Data of AEROSIL® Fumed Silica

Hydrophilic AEROSIL® Fumed Silica

Test methods	AEROSIL® 90	AEROSIL® 130	AEROSIL® 150	AEROSIL® 200	AEROSIL® 300	AEROSIL® 380	AEROSIL® OX 50	AEROSIL® TT 600	AEROSIL® MOX 80	AEROSIL® MOX 170	AEROSIL® COK 84	AEROXIDE® Alu C	AEROXIDE® TiO ₂ P 25	
Behavior towards water	hydrophilic													
Appearance	-fluffy white powder -													
BET surface area BET ¹⁾	m ² /g	90 ± 15	130 ± 25	150 ± 15	200 ± 25	300 ± 30	380 ± 30	50 ± 15	200 ± 50	80 ± 20	170 ± 30	185 ± 30	100 ± 15	50 ± 15
Average primary particle size	nm	20	16	14	12	7	7	40	40	30	15	-	13	21
Tapped density ²⁾ <i>approx. value</i>	g/L	80	50	50	50	50	50	130	60	60	50	50	50	130
Standard material	g/L	80	50	50	50	50	50	130	60	60	50	50	50	130
Densified material (suffix „V“)	g/L	120	120	120	120	120	120							
Densified material (suffix „VV“)	g/L			50/75	50/75/120	50/75/120								
Loss on drying ³⁾ (2 h at 105 °C) when leaving the plant	wt. %	≤ 1.0	≤ 1.5	≤ 0.5 ⁹⁾	≤ 1.5	≤ 1.5	≤ 2.0	≤ 1.5	≤ 2.5	≤ 1.5	≤ 1.5	≤ 1.5	≤ 5.0	≤ 1.5
Loss on ignition ^{4) 7)} (2 h at 1000 °C)	wt. %	≤ 1.0	≤ 2.5	≤ 1.0	≤ 1.0	≤ 2.0	≤ 2.5	≤ 1.0	≤ 2.5	≤ 1.0	≤ 1.0	≤ 1.0	≤ 3.0	≤ 2.0
pH-value ⁵⁾ (4% aqueous dispersion)		3.7 - 4.7	3.7 - 4.7	3.7 - 4.7	3.7 - 4.7	3.7 - 4.7	3.7 - 4.7	3.8 - 4.8	3.6 - 4.5	3.6 - 4.5	3.6 - 4.5	3.6 - 4.3	4.5 - 5.5	3.5 - 4.5
SiO ₂ ⁸⁾	wt. %	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.3	≥ 99.3	82 - 86	≥ 0.1	≤ 0.2
Al ₂ O ₃ ⁸⁾	wt. %	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.08	≤ 0.05	0.3 - 1.3	0.3 - 1.3	14 - 18	≥ 99.6	≤ 0.3
Fe ₂ O ₃ ⁸⁾	wt. %	≤ 0.003	≤ 0.003	≤ 0.003	≤ 0.003	≤ 0.003	≤ 0.003	≤ 0.01	≤ 0.003	≤ 0.01	≤ 0.01	≤ 0.1	≤ 0.2	≤ 0.01
TiO ₂ ⁸⁾	wt. %	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.1	≥ 99.5
HCl ^{8) 10)}	wt. %	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.1	≤ 0.5	≤ 0.3
Sieve residue ⁶⁾ (by Mocker, 45 µm)	wt. %	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.2	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.05
Unit weight ¹²⁾ (netto)	kg	10	10	10	10	10	10	10	10	10	10	10	10	10

The data have no binding force.

1) in acc. to DIN 66131

2) in acc. to DIN EN ISO 787/11, JIS K 5101/18 (not sieved)

3) in acc. to DIN EN ISO 787/2, ASTM D 280, JIS K 5101/21

4) in acc. to DIN EN ISO 3262-20, ASTM D 1208, JIS K 5101/23

5) in acc. to DIN EN ISO 787/9, ASTM D 1208, JIS K 5101/24

6) in acc. to DIN EN ISO 787/18, JIS K 5101/20

7) based on material dried for 2 hours at 105 °C

8) based on material ignited for 2 hours at 1000 °C

9) special moisture-protective packaging

10) HCl-content is part of the ignition loss

11) AEROSIL® V-Grades will be delivered in paperbags of 20 kg

12) AEROSIL® VV-Grades are presently only available from the production plant in Rheinfelden by now

Hydrophobic AEROSIL® Fumed Silica

Test methods		AEROSIL® R 972	AEROSIL® R 974	AEROSIL® R 202	AEROSIL® R 805	AEROSIL® R 812	AEROSIL® R 812 S	AEROSIL® R 104	AEROSIL® R 106	AEROSIL® R 8200	AEROSIL® R 816	AEROXIDE® TiO ₂ T 805
Behavior towards water		hydrophobic										
Appearance		-fluffy white powder -										
BET surface area <i>BET</i> ¹⁾	m ² /g	110 ± 20	170 ± 20	100 ± 20	150 ± 25	260 ± 30	220 ± 25	150 ± 25	250 ± 30	160 ± 25	190 ± 20	45 ± 10
Average primary particle size	nm	16	12	14	12	7	7	12	7	-	12	21
Tapped density ²⁾ <i>approx. value</i>												
Standard material	g/L	50	50	50	50	50	50	50	50	140	40	200
Densified material (suffix „V“)	g/l	90	90					90				
Densified material (suffix „VV“)	g/l			60/90 ¹³⁾	60/90 ¹³⁾	60/90 ¹³⁾	90 ¹³⁾					
Loss on drying ³⁾ (2 h at 105 °C) when leaving the plant	wt. %	≤ 0.5	≤ 0.5	≤ 2.0	≤ 0.5	≤ 0.5	≤ 0,5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 1.0	≤ 1.0
Loss on ignition ⁴⁾⁷⁾ (2 h at 1000 °C)	wt. %	≤ 2	≤ 2	4 - 6	5 - 7	1.0 - 2.5	1.5 - 3.0	1.0 - 2.5	1.0 - 2.5	2.5 - 3.5	2.0 - 4.0	≤ 5.0
C-content	wt. %	0.6-1.2	0.7-1.3	3.5-5.0	4.5-6.5	2.0-3.0	3.0-4.0	1.0 - 2.0	1.5 - 3.0	2.0 - 4.0	1.2 - 2.2	2.7 - 3.7
pH-value ^{5) 10)} (4% aqueous dispersion)		3.6 - 4.4	3.7-4.7	4 - 6	3.5 - 5.5	5.5 - 7.5	5.5 - 7.5	≥ 4.0	≥ 3.7	≥ 5.0	4.0 - 5.5	3.0 - 4.0
SiO ₂ ⁸⁾	wt. %	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≤ 2.500
Al ₂ O ₃ ⁸⁾	wt. %	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	
Fe ₂ O ₃ ⁸⁾	wt. %	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.010
TiO ₂ ⁸⁾	wt. %	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≥ 97.00
HCl ¹¹⁾	wt. %	≤ 0.05	≤ 0.1	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.025	≤ 0.02	≤ 0.025	≤ 0.025	≤ 0.025	
Unit weight ¹²⁾ (<i>netto</i>)	kg	10	10	10	10	10	10	10	10	15	10	20

The data have no binding force.

¹⁾ in acc. to DIN 66131

²⁾ in acc. to DIN EN ISO 787/11, JIS K 5101/18 (not sieved)

³⁾ in acc. to DIN EN ISO 787/2, ASTM D 280, JIS K 5101/21

⁴⁾ in acc. to DIN EN ISO 3262-20, ASTM D 1208, JIS K 5101/23

⁵⁾ in acc. to DIN EN ISO 787/9, ASTM D 1208, JIS K 5101/24

⁷⁾ based on material dried for 2 hour at 105 °C

⁸⁾ based on material ignited for 2 hours at 1000 °C

¹⁰⁾ in Water: methanol = 1 : 1

¹¹⁾ HCl content is part of the ignition loss

¹²⁾ AEROSIL® V-Grades will be delivered in paperbags of 15 kg

¹³⁾ AEROSIL® VV-Grades will be delivered in paperbags of 15 kg

12 Physical and Chemical Data of SIPERNAT®

Physical and Chemical Data of the Evonik Precipitated Silicas

Test methods		SIPERNAT® 320 DS	SIPERNAT® 383 DS	SIPERNAT® 500 LS	SIPERNAT® D 10	SIPERNAT® D 17
Behaviour towards water		hydrophilic			hydrophobic	
Appearance		-fluffy white powder -				
BET surface area <i>BET</i> ¹⁾	m ² /g	175	170	450	90	100
Average primary particle size ⁸⁾	µm	5.0 ⁸⁾	5.0 ⁸⁾	4.5 ⁸⁾	4.5 ⁸⁾	7 ⁸⁾
Tapped density ²⁾ <i>approx. value</i>	g/L	75	75	75	100	150
Loss on drying ³⁾ <i>(2 h at 105 °C) when leaving the plant</i>	wt. %	6.0	6.0	3.0	3.0	6.0
Loss on ignition ^{4) 9)} <i>(2 h at 1000 °C)</i>	wt. %	5.0	5.0	5.0 ¹²⁾	7.0 ¹³⁾	1.0 - 2.5
pH-value ⁵⁾ <i>(5% aqueous dispersion)</i>		6.3	8.3	6.0	10.3 ¹¹⁾	8.0 ¹¹⁾
DBP absorption ^{6) 9)}	g/100 g	235	230	325	230	225
SiO ₂ ⁸⁾	wt. %	98.0	98.0	98.5	98.0	99.5
Na ₂ O ¹⁰⁾	wt. %	1.0	1.2	0.6	1.0	1.0
Fe ₂ O ₃ ⁸⁾	wt. %	0.03	0.03	0.03	0.03	0.03
Sulphate as SO ₃	wt. %	0.8	0.8	0.7	0.8	0.8
Sieve residue ⁷⁾ <i>(by Mocker, 45 µm)</i>	wt. %	0.01	0.01	0.01	0.01	0.1
Unit weight ¹²⁾ <i>(netto)</i>	kg	15	12.5	10	15	15

¹⁾ in accordance with ISO 5794/1, annex D

²⁾ in accordance with DIN EN ISO 787/11

³⁾ in accordance with DIN EN ISO 787/2, ASTM D 280, JIS K 5101/21

⁴⁾ in accordance with ISO 3262/11, ASTM D 1208

⁵⁾ in accordance with DIN EN ISO 787/9, ASTM D 1208

⁶⁾ in accordance with DIN 53601, ASTM D 2414

⁷⁾ in accordance with DIN EN ISO 787/18

⁸⁾ in accordance with ASTM C 690-1392 Coulter multisizer, 100 µm capillare

⁹⁾ based on the substance which has been dried for 2 hours at 105 °C

¹⁰⁾ based on the substance which has been dried for 2 hours at 1000 °C

¹¹⁾ in water: methanol = 1:1

¹²⁾ contains approx. 3% chemically bonded carbon

¹³⁾ contains approx. 2% chemically bonded carbon

The data have no binding force.

These typical values provide a general description of the product and should not be used as product specifications.

This information and any recommendations, technical or otherwise, are presented in good faith and believed to be correct as of the date prepared. Recipients of this information and recommendations must make their own determination as to its suitability for their purposes. In no event shall Evonik assume liability for damages or losses of any kind or nature that result from the use of or reliance upon this information and recommendations. EVONIK EXPRESSLY DISCLAIMS ANY REPRESENTATIONS AND WARRANTIES OF ANY KIND, WHETHER EXPRESS OR IMPLIED, AS TO THE ACCURACY, COMPLETENESS, NON-INFRINGEMENT, MERCHANTABILITY AND/OR FITNESS FOR A PARTICULAR PURPOSE (EVEN IF EVONIK IS AWARE OF SUCH PURPOSE) WITH RESPECT TO ANY INFORMATION AND RECOMMENDATIONS PROVIDED. Reference to any trade names used by other companies is neither a recommendation nor an endorsement of the corresponding product, and does not imply that similar products could not be used. Evonik reserves the right to make any changes to the information and/or recommendations at any time, without prior or subsequent notice.

AEROSIL®, SIPERNAT®, Dynasylan® and PRINTEX® are registered trademarks of Evonik Industries AG or its subsidiaries.



EVONIK
INDUSTRIES

Europe / Middle-East /
Africa / Latin America

Evonik Resource Efficiency GmbH

Business Line Silica
Rodenbacher Chaussee 4
63457 Hanau
Germany

PHONE +49 6181 59-12532

FAX +49 6181 59-712532

ask-si@evonik.com

www.evonik.com

North America

Evonik Corporation

Business Line Silica
299 Jefferson Road
Parsippany, NJ 07054-0677
USA

PHONE +1 800 233-8052

FAX +1 973 929-8502

ask-si-nafta@evonik.com

Asia Pacific

Evonik (SEA) Pte. Ltd.

Business Line Silica
3 International Business Park
#07-18, Nordic European Centre
Singapore 609927

PHONE +65 6809-6877

FAX +65 6809-6677

ask-si-asia@evonik.com

TB 63-1 JUL15

Evonik. Power to create.