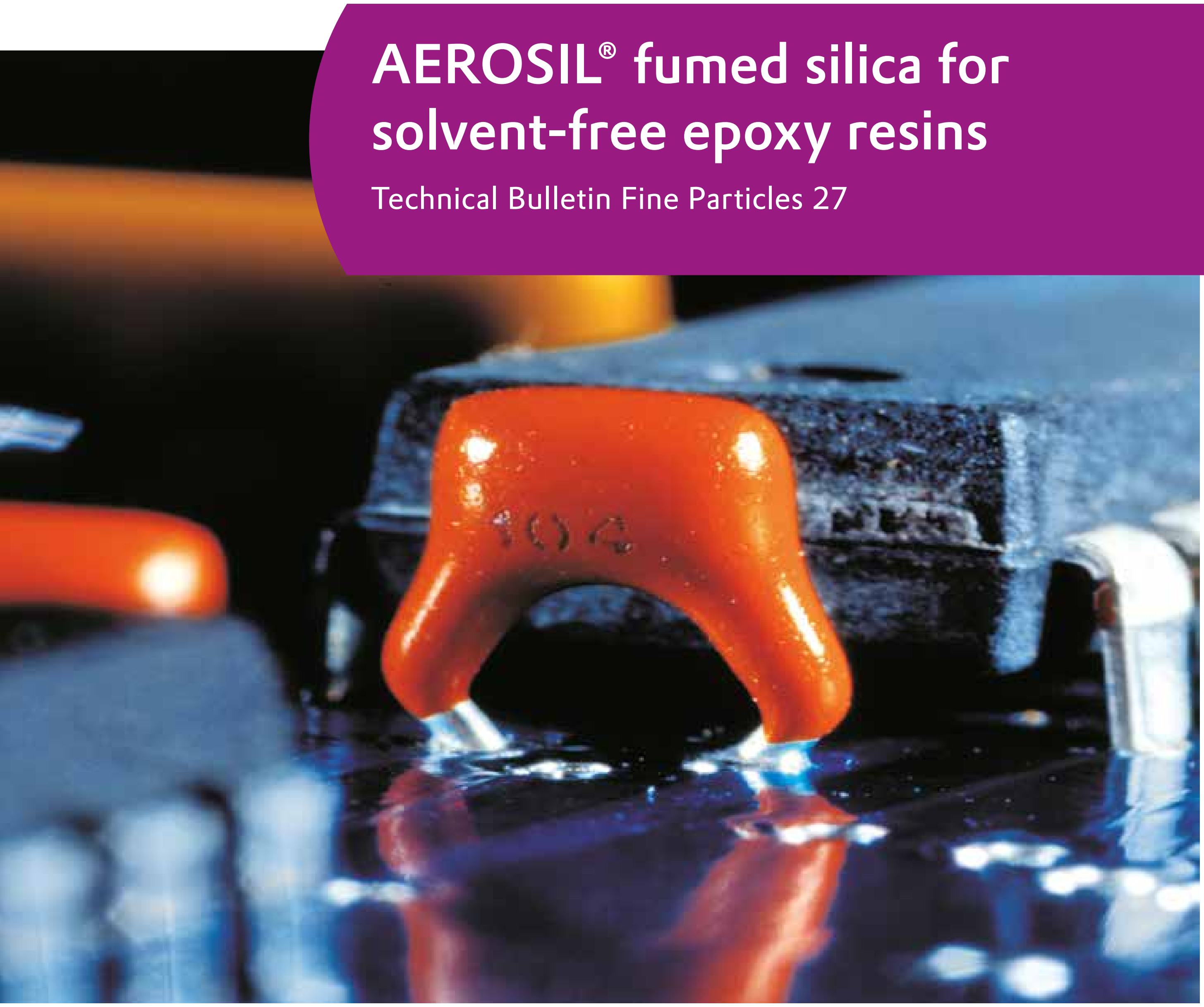
AEROSIL® fumed silica for solvent-free epoxy resins

Technical Bulletin Fine Particles 27



Evonik. Power to create.

AEROSIL® fumed silica is a submicron amorphous silica which has been used successfully for decades as a thickening agent and thixotrope in liquid systems. It is also used to adjust the rheological properties of epoxy resins.

Two products that have been developed, the hydrophobic fumed silica grades AEROSIL® R 202 and AEROSIL® R 805, also serve as rheological aids to provide effective, stable thickening and thixotropy of problematic epoxy systems.

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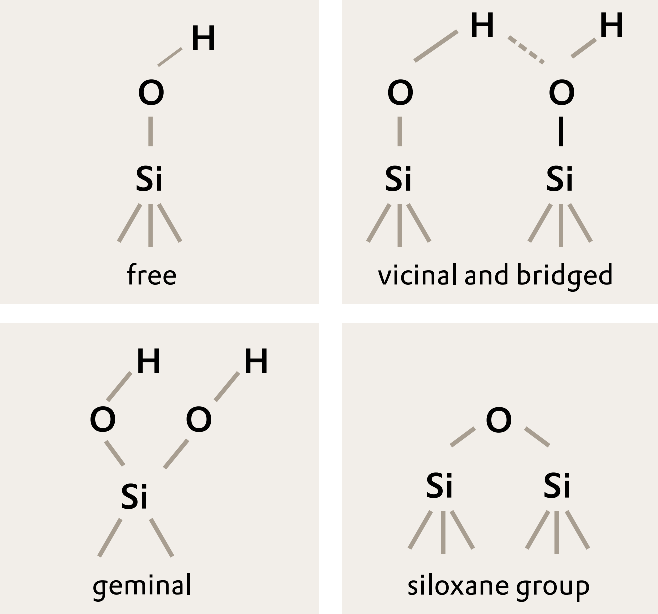
1 General information

1.1 AEROSIL® fumed silica

AEROSIL® fumed silica is a highly dispersed, amorphous, very pure silica which is produced by high temperature hydrolysis of silicon tetrachloride in an oxyhydrogen gas flame. The primary particles are spherical and free of pores. The primary particles in the flame interact to develop aggregates which join together reversibly to form agglomerates. **Figure 1** shows a transmission electron micrograph (TEM) of AEROSIL® 300 in which the primary particles, aggregates and agglomerates can be clearly seen. The average diameters of the primary particles lie between 7 and 40 nm according to AEROSIL® fumed silica grade, while the specific surface areas range accordingly between 50 and 380 m²/g. Siloxane and silanol groups are situated on the surface of the AEROSIL® fumed silica particles. The latter are responsible for the hydrophilic behavior of untreated AEROSIL® fumed silica **Figure 2** shows the surface groups of hydrophilic AEROSIL®.

Figure 2 Possible surface groups of hydrophilic silicas



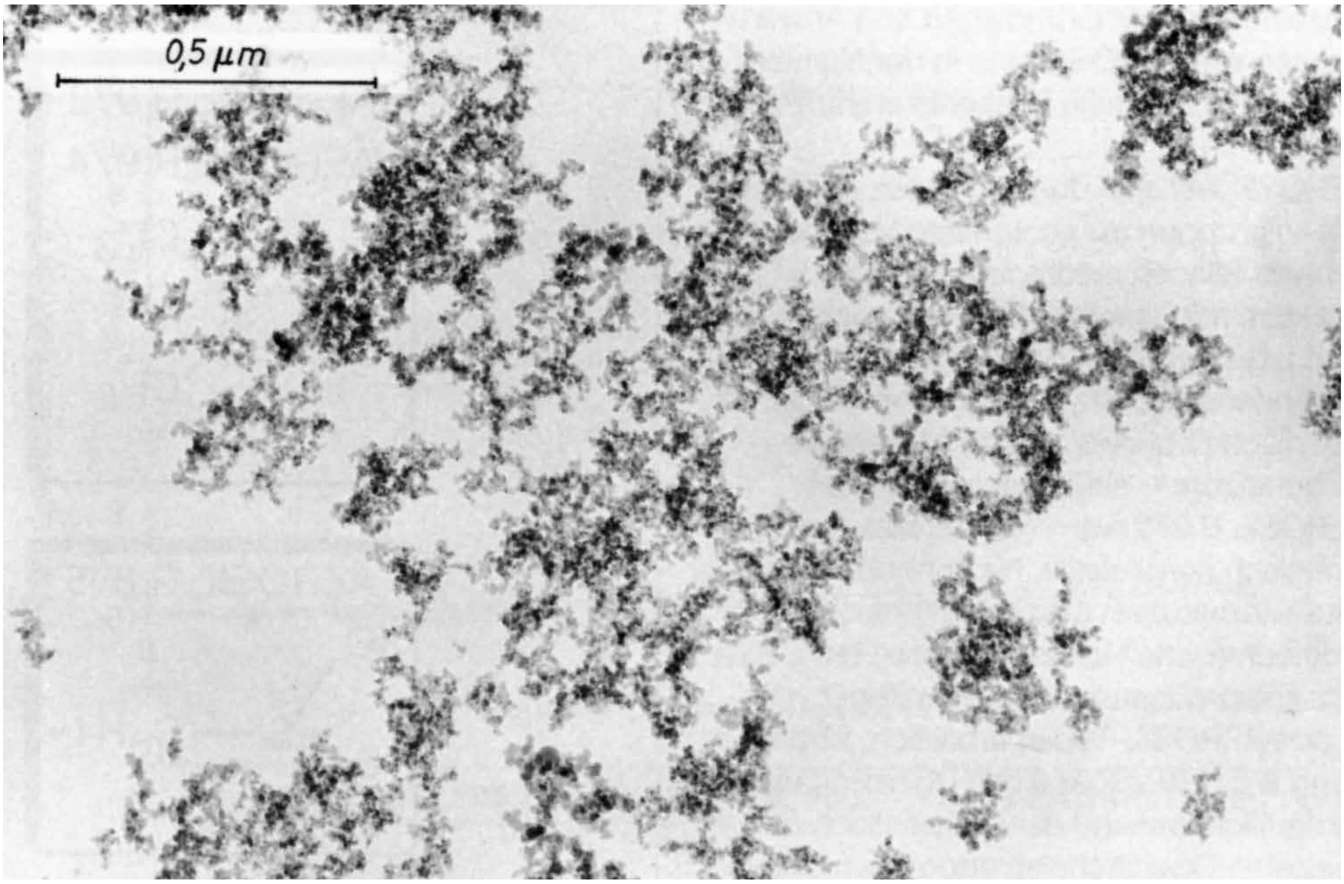


Figure 1 Transmission electron micrograph (TEM) of AEROSIL® 300

Details on the production and surface chemistry of AEROSIL® fumed silica are contained in in brochure No. 11 in this series of Technical Bulletin Fine Particles (1).

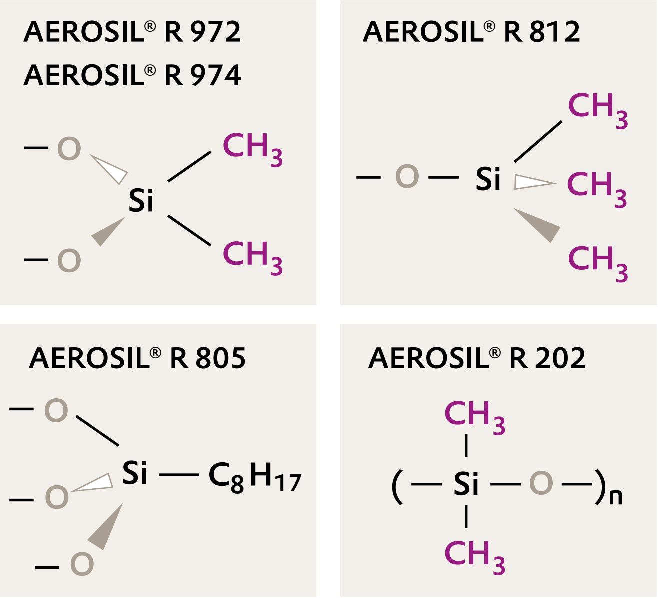
AEROSIL® fumed silica can be surface-modified by reacting the silanol groups with suitable compounds; for example, AEROSIL® R 972 is derived through the reaction with dimethyldichlorosilane. This substance which is hydrophobic due to bound hydrolysis–stable methyl groups, was introduced to the market in 1962 as the first commercially produced hydrophobic silica.

Figure 3 shows a general schematic view of the surface groups on the different hydrophobic grades.

Hydrophilic and hydrophobic grades of AEROSIL® have proved successful for use in numerous fields of application. With regard to plastics, the following functions should be mentioned:

- **Reinforcing filler,**
- **Thickening and thixotropic agent**
- **Anti-settling agent, and**
- **Free-flow aid.**

Figure 3 Hydrophobic AEROSIL® fumed silica grades and their surface groups



In contrast to silicas of mineral origin, meaning quartz powder which is used mainly as a „filler" in the true sense of the word, the desired effects can be obtained by adding only relatively small amounds of synthetic silicas.

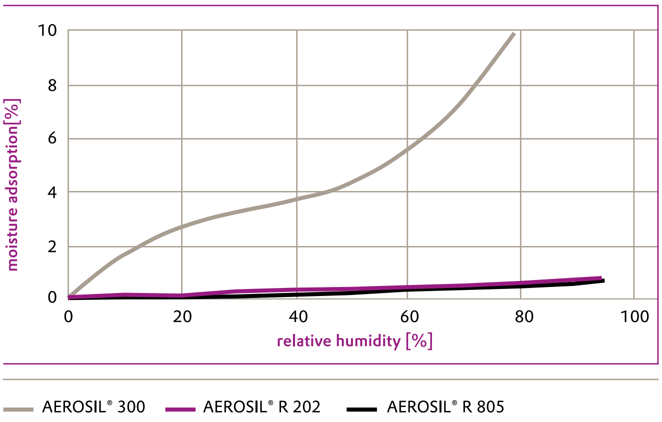
A general view of the application of AEROSIL® fumed silica and uses in plastics are specifically shown in (2).

The technical properties of a silica may be optimized for use in specific fields of application by the way in which the surface is modified; this has resulted in the development of AEROSIL® R 202 and AEROSIL® R 805.

Theoretical considerations have led to the assumption that a surface coating composed of longer–chain, hydrophobic groups should permit a more effective adjustment of the rheological characteristics in many liquid polymer systems –especially in epoxy resins. AEROSIL® R 202 which has polydimethylsiloxane groups anchored to the surface and AEROSIL® R 805 which is rendered hydrophobic with octyl groups confirm this to a great degree.

The hydrophobic character of these two after treated grades of AEROSIL® fumed silica can be compared with AEROSIL® 300 by means of water vapor adsorption with increasing humidity in the air (**Figure 4**).

Figure 4 Adsorption isotherms of various AEROSIL® fumed silica grades at room temperature



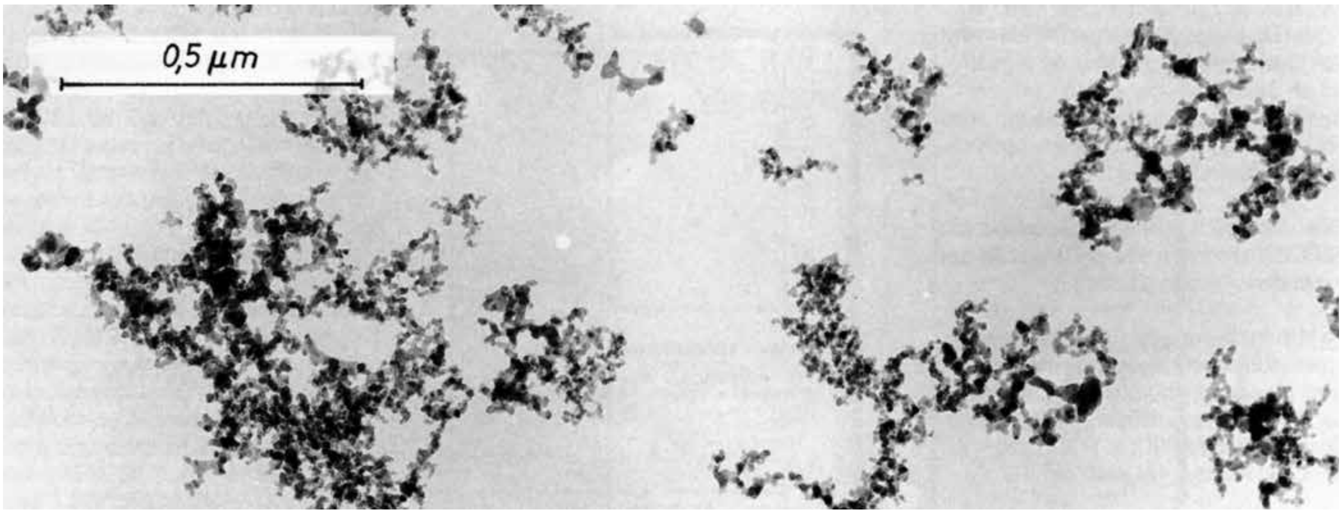


Figure 5 Transmissions electron micrograph (TEM) of AEROXIDE® Alu C

1.2 AEROXIDE® Alu C

AEROXIDE® Alu C is produced according to the AEROSIL® fumed silica process by high-temperature hydrolysis of aluminium chloride in an oxyhydrogen gas flame in the following stoichiometric ratios:

$$4\ AlCl_3 + 6\ H_2 + 3\ O_2 - 2\ Al_2O_3 + 12\ HCl$$

AEROXIDE® Alu C has a mean primary particle size of 13 nm and a specific surface area of approximately 100 m^2/g. Similar to AEROSIL® fumed silica, these primary particles have no inner surface. **Figure 5** shows a transmissions-electron-microscopic photo of AEROXIDE® Alu C.

In powder coatings which are electrostatically applied, AEROXIDE® Alu C improves flowability and due to it´s positive changeability it improves the application of powder coating by the Tribo method. In powder coatings which tend to agglomerate and stick together, AEROXIDE® Alu C can generally be used as free-flow agent.

1.3 Epoxy Resins – Significance and Usage

The technically most important epoxy resins are produced through condensation of 2,2-bis-(4-hydroxyphenyl) propane, also called bisphenol A, and epichlorohydrin in an alkaline environment. It yields according to the used equivalents of both educts glycidylether (bisphenol A Epoxy) with a variable molar mass.

During recent years epoxy resins based on bisphenol F, novolac-epoxy resins as well as cycloaliphatic and heterocyclic epoxy resins have gained significance.

Epoxy resins by themselves are poor film formers and yield brittle layers. Therefore a curing agent is necessary.

A variety of curing agents are used, including amines, polyamides, polyamidoamines and carboxylic acid anhydrides. Amine hardeners are also varied and include the following polyamines:

- **aliphatic,**
- **cycloaliphatic** and
- **aromatic**

Curing occurs without separation of components and can be exothermic. In the cure a hydrogen atom is added to the epoxy group whereby a hydroxyl group is created.

Epoxy resin formulations can be one- or two-component systems. With the choice of resins and hardeners as well as other components, the final properties of epoxy resin formulations can be improved to a great extent. Generally epoxy resins show the following advantages as opposed to other plastics (3, 4):

- **very good adhesion to a variety of substrates**
- **good sealing ability with low shrinkage**
- **high mechanical and thermal properties**
- **good electrical insulating properties**
- **good chemical resistance**

Table 1 shows a general view of the wide ranges of applications for epoxy resin formulations (5). Each of these applications can be improved by use of AEROSIL® fumed silica as rheological additive.

- **Room temperature-cure coatings for corrosion protection and for construction industry**
- **Electrocasting**
- **Injection resins**
- **Epoxy cement and mortar**
- **Adhesives**
- **Tool repair resins**
- **Powder coatings**
- **Baked enamels**

and other specialized applications.

The most important ranges of application are for Protective Coatings (approximately 60 %) and so called "formulated Systems" (40 % (6)). Included in this class are applications such as electro- and electronic applications, application in tool manufacturing as well as composite materials. Protective coatings belong to the area of solvent-containing systems and include coating for food contact, marine, automotive and industrial end uses.

2 AEROSIL® fumed silica in solvent free epoxy resins

2.1 Rheological problems with epoxy resin formulations

In epoxy resin formulations various rheological effects (8, 9) are observed prior to during processing.

Prior to application:

- **Adjustment of the processing viscosity of the liquid epoxy resin**
- **Thickening of the hardening components**
- **Adjustments to resin and hardening components to improve shelf life stability**
- **Prevention of settling of fillers**
- **Consistent rheological properties after temperature increase through shearing or filling procedures.**

During and after the application:

- **Change of rheological properties over varied process shear rates.**
- **Prevention of sedimentation of fillers during curing.**
- **Change of visco–elasticity of formulations**
- **Sagging performance of polymer layers on vertical surfaces (14)**

Most of the known rheological problems appear during application and in many cases are inter-related. Good thixotropy even under high shear rates is demanded of the epoxy resin systems. Additionally, the good thixotropy is required during curing and when formulations are applied to vertical surfaces.

2.2 Mechanism of thickening and thixotropy with AEROSIL® fumed silica in liquids and epoxy resins

AEROSIL® fumed silica is successfully used as a thickening and thixotropic filler in liquids. The effect is distinctiy marked in non-polar systems. Polarity is understood as a capability of fluid molecules to form hydrogen bonds.

The thickening and thixotropy effect can be explained with the formation of a three dimensional network of AEROSIL® fumed silica particles in the system. By shaking and stirring, the network is broken down, depending on the intensity and duration of the stress. Furthermore the viscosity is reduced accordingly. At rest, the network reforms and viscosity rebounds in the original value. The mechanism is shown schematically in **Figure 6**. **Figure 7** illustrates the concept of thixotropy.

The interaction between the silanol groups of various AEROSIL® fumed silica particles are responsible for the formation of stable networks. In non-polar fluids such as hydrocarbons or polydimethyl-siloxanes, the hydrogen bond between AEROSIL® fumed silica particles is maximized. When fluid molecules (owing to their polarity) show an affinity to the silanol groups, a solvation of the AEROSIL® fumed silica particles and a de-stabilization of the thixotropic network occur. For this reason the thickening of polar fluids such as ethanol or water is only possible with relatively large quantities of hydrophilic AEROSIL® fumed silica grades.

Figure 6 Schematic graph of the shear thinning effect of AEROSIL® fumed silica particles in fluids

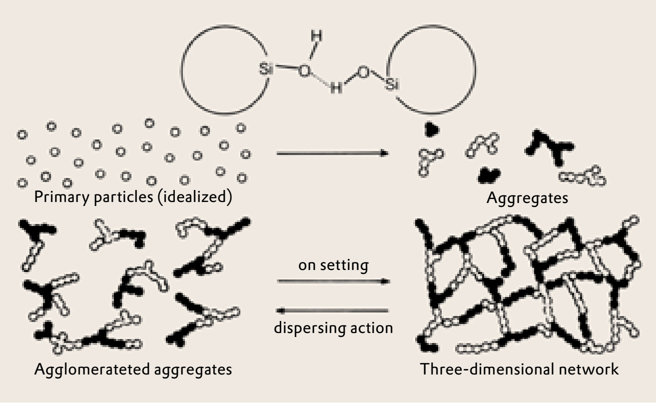
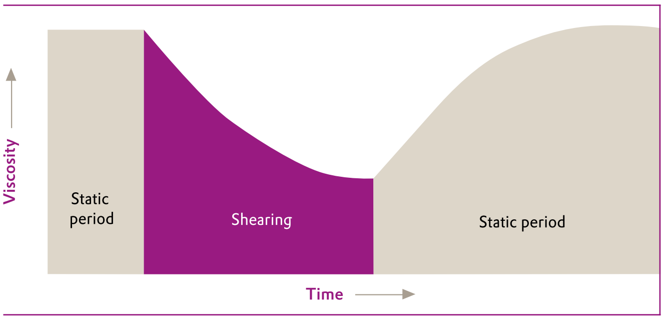


Figure 7 Thixotropy = decrease in the viscosity during the shearing time, and increase again during the static period (schematic)



In many polar fluids one can prevent this disadvantage by using the special type of AEROSIL® COK 84. This product consists of AEROSIL® 200 and AEROXIDE® Alu C. In polar systems a network is also formed. However, its origin is based on the interaction between the negatively charged AEROSIL® 200 and the positively charged AEROXIDE® Alu C-particles. Since this mechanical is less sensitive to the polarity of a fluid, water, dimethly-sulfoxide or dimethyl formamide can be thixed with AEROSIL® COK 84, also see 3.

The presence of small quantities of compounds containing hydroxyl groups in non-polar or partial polar fluids produces a synergetic effect. The network of AEROSIL® fumed silica particles is additionally bridged in this case. However, a reduction in viscosity occurs when the bridged agent exceeds small quantities. Hydroxyl or amino groups positively influence the thickening and thixotropy effect in certain systems.

Owing to their polarity, solvent free epoxy resins cannot be optimally thickened with hydrophilic AEROSIL® fumed silica. After the addition of certain polyamines a deterioration of the rheological properties during the potlife occurs. The initial rise in viscosity that is first observed is due to an additional linkage of AEROSIL® fumed silica particles through the multi-functional amino compounds and produces a reinforcement of the three-dimensional network. However, the hydrophilic AEROSIL® fumed silica particles are increasingly solvated by polymer molecules containing hydroxyl groups which originate during the curing reaction. With more hydroxyl groups forming the network is degraded and the viscosity and thixotropy decreases.

With the development of AEROSIL® R 202 and AEROSIL® R 805, stable thickening and thixotropy in epoxy resins can be achieved. With the addition of an amine hardener the viscosity value and thixotropy remain largely constant during the hardening.

On the surface of the particles of AEROSIL® R 202 and AEROSIL® 805 are fixed longer-chained hydrophobic groups. These shield the remaining silanol groups and prevent undesired wetting. The remaining silanol groups as well as the longer-chained hydrophobic groups are responsible for the thickening and thixotropic effect with AEROSIL® R 202 and AEROSIL® R 805. As explanation for the thickening and thixotropic effect of hydrophobic AEROSIL® fumed silica grades a three-dimensional network can also be used.

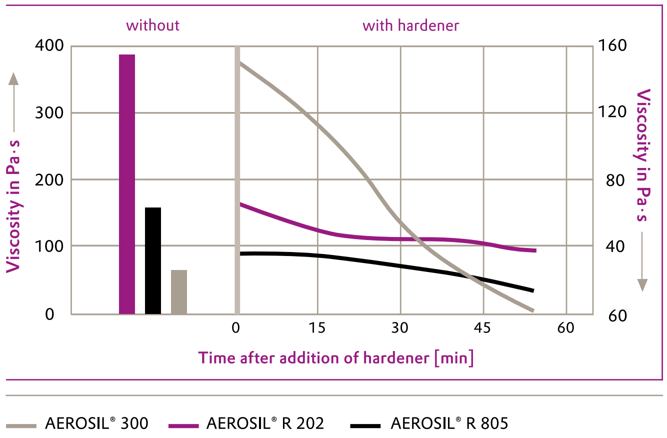
Figure 8 shows as example the thickening effect of various AEROSIL® fumed silica grades in a low-viscous reactive thinned epoxy resin before and after the addition of a mixture of polyaminoamide as curing agent and a tertiary amine as accelerator.

In systems thickened with hydrophilic AEROSIL® 300, a decrease in the viscosity of the hardener resin mixture is observed in many cases. In systems thickened with hydrophobic AEROSIL® grades R 202 and R 805, the viscosity of the hardener resin mixture remains relatively constant during application.

Method of operation for the tests shown in **Figure 8** and other figures.

Direct addition of the silica to the epoxy resin. Total wetting of the silica with resin by means of the lab dissolver (∅ 5 cm, cowles-blade) at 1000 rpm for 1 min. and dispersion with lab dissolver at 3000 rpm for 5 min. Followed by deaeration of samples.

Figure 8 Viscosity drop of an epoxy resin (ARALDIT M, Huntsman) with 5,6 % AEROSIL® fumed silica before and 3.8 % AEROSIL® fumed silica after the curing agent and accelerator addition



Storage of the resin-silica mixture for 1.5 h at 25 °C, followed by mixing into the hardening components which were tempered at 25 °C and mixed for 1 min. at 1000 rpm. Measurement of the viscosities with a Brookfield-Rotation-viscometer at 2.5 rpm. In each case directly after the addition of the hardener as well as after the stated times in the diagrams (**Figure 9**).

Figure 9
Rotation viscometer DV-II of the Brookfield Engineering Laboratories, Inc., 240 Cushing St., Stoughton, MA 02072 USA

2.3 Dispersion of AEROSIL® fumed silica in epoxy resins

The process of dispersion consists generally of an alternating dispersion and wetting of the powdery components in the liquid resin (10). The aim of dispersion of AEROSIL® fumed silica into epoxy resins is to split the silica agglomerates into aggregates with medium effective aggregate sizes of approximately 100 - 300 nm, so that these are homogenously dispersed into the resins. Epoxy resins thickened with AEROSIL® fumed silica show that with sufficient dispersion very good rheological properties and storage stability can be obtained.

For the dispersion of AEROSIL® fumed silica in epoxy resins, dissolvers, planetary mixers, triple roller mills, and kneaders can be used. Propeller stirrers are suited only for blending. Due to the low shearing stress they produce, they are less suited for the process of dispersion.

Figure 10
Lab dissolver blade (Cowles-Dissolver, Co., Morehouse, N. Y.)

Very high shear stresses can be obtained with a triple roller mill. However, these have the disadvantage of being discontinous and energy intensive. Dissolvers and planetary mixers have (in addition to the continuous incorporation and the low expenditure of energy) the advantages of very high productivity and dispersion capacity.

Figure 10 shows a lab dissolver with a Cowles blade as it was used for the experiments described in this brochure (process of testing see page 10). In **Figure 11** a lab planetary mixer is shown which can be used for dispersion of higher viscosity filled epoxy resins.

Figure 11
Lab planetary dissolver with vacuum- and inert gas equipment
(Hermann Linden GmbH & Co., KG, 51709, Marienheide, Germany)

The principal dispersion of the silica occurs near the cowles-blade periphery. Due to the difference of speed between the fast running cowles-blade and that of the slower moving sweepblade, high shearing speeds and therefore also high shearing forces, respectively, shearing stresses will be obtained (11). Under these conditions, silica agglomerates can easily be converted into silica aggregates.

Optimal tip speeds and geometrical dimensions for dissolvers are given at the next page.

tip speed m/s: 8–20
Diameter stirring blade /
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**

2.4 Thickening and thixotropy of various epoxy resins

For the experiments described in this report the raw materials listed in **Table 2** were used. **Figures 12**, **13**, and **14** show the thickening performance of the five tested AEROSIL® fumed silica grades in the plasticized DGEBA resin, Standard DGEBA resin, reactively diluted DGEBA resin. The same trend of thickening performance was found in all known epoxy resins. The AEROSIL® fumed silica grades R 202 and R 805 thicken the epoxy resins significantly better than the other AEROSIL® fumed silica grades. In comparison, in epoxy systems the hydrophilic silica AEROSIL® 300 shows little to no thickening effect.

This result is remarkable at first glance, because AEROSIL® 300 has the highest specific surface area among the tested silicas. In general for hydrophilic The AEROSIL® fumed silica grades, higher thickening of fluid systems can be adjusted with higher surface area (13). However, in comparing the thickening effect of various AEROSIL® fumed silica grades in epoxy, it is obvious that the surface chemistry has a greater influence than the surface area.

Figure 12 Comparisation of thickening effect of different AEROSIL® fumed silica grades with a concentration of 4 % in a plasticized DGEBA resin at room temperature.

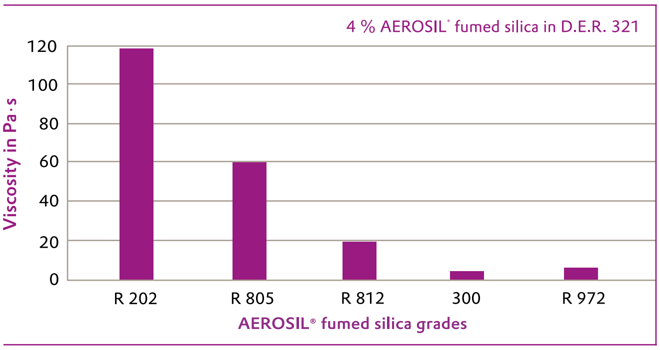


Table 2 Raw materials used in the evaluation

All treated tested silicas have specific surfaces of < 300 m^2/g.

Silicas
- AEROSIL® 300
- AEROSIL® R 202
- AEROSIL® R 805
- AEROSIL® R 812
- AEROSIL® R 972

Epoxy resins
- EPIKOTE 216
- D.E.R. 321
- ARALDIT M
- EUREPOX 710, -730, -776, -784
- RUTAPOX VE 3161

Hardeners
- Polyaminoamid (EUREDUR 250)
- Polyaminoimidazolin (VERSAMID 140,-145)
- Cycloaliphatic polyamine (EUREDUR 43)
- Polyamine (EUREDUR 10, -12, -16, -34)
- Aromatic Amine (EUREDUR 80, -81 S)
- Tertiary Amine as catalyst (HY 960, EUREDUR 13)
- Mercaptan hardener (CAPCURE 3-800)

As already indicated in section 2.2, the hydrophilic AEROSIL® fumed silica particles are solvated by polar epoxy resins. The threedimensional network cannot develop and therefore the thickening effect is inadequate in comparison to the hydrophobic AEROSIL® fumed silica.

The significant difference in the thickening performance in all three epoxy resins shows that the surface chemistry plays a big influence on the rheological properties. On the surface of AEROSIL® R 202 and AEROSIL® R 805, long-chain molecules are chemically bonded (compare **Figure 3**). Polysiloxane chains and long-chain organic silanes have proven to be very effective. The thickening performance of silicas which were modified with short-chain silanes have proven to be less effective. AEROSIL® R 972 and AEROSIL® R 812 were hydrophobized with methyl silanes. Obviously, "volume ratio" substituents are decisive for the thickening of epoxy resins.

Figure 13 Comparison of thickening effect of various AEROSIL® fumed silica grades with a concentration of 4 % in a standard DGEBA-resins at room temperature

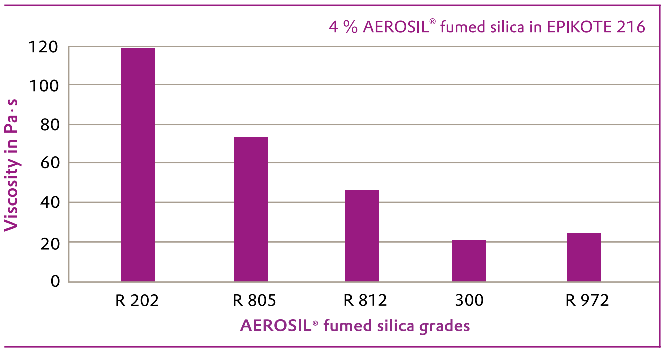
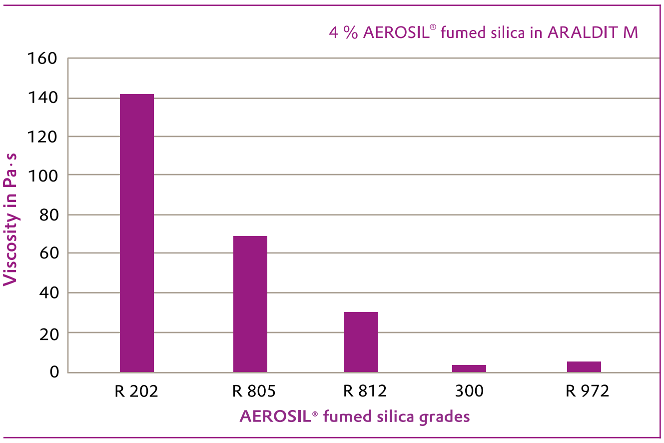


Figure 14 Comparison of thickening effect of various AEROSIL® fumed silica grades at a concentration of 4 % in a reactively diluted DGEBA-resin at room temperature

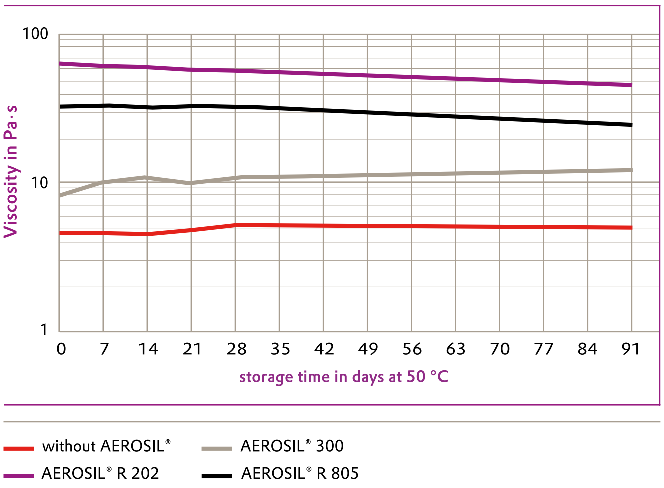


2.4.1 Shelf life of epoxy resins containing silica

For such investigations the AEROSIL® fumed silica grades AEROSIL® R 805, AEROSIL® R 202 and AEROSIL® 300 are incorporated into the bisphenol A resin Epikote 216 and stored for 90 days at 50 °C. For comparison purposes a sample of the pure resin was tested alongside.

During storage, the viscosity of the thickened epoxy resin systems hardly change with storage time, as **Figure 15** shows.

Figure 15 Viscosity performance of EPIKOTE 216 thickened with various AEROSIL® fumed silica grades (concentration 4 %) at 50 °C as function of the storage time

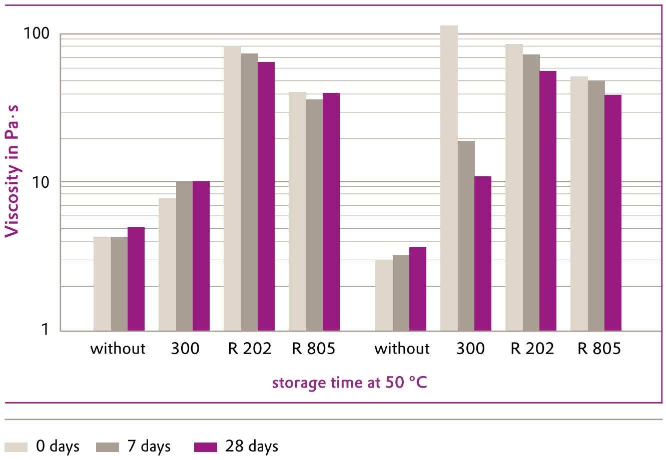


2.4.2 Influence of silanes on rheology of epoxy resins containing silica

For the improvement of adhesion, frequently bi-functional silanes are applied in epoxy adhesives. These are usually Gammaglycidoxypropyl-trimethoxysilanes, e.g. Dynasylan® GLYMO. The addition of this silane can decisively change the rheology of epoxy resins containing silica. In pure epoxy resins the addition of 2 parts of silanes causes a decrease in the viscosity, as seen in **Figure 16**. This is due to a dilution effect.

The epoxy resin containing hydrophilic silica shows a higher viscosity after the addition of silane. This increases the viscosity of the epoxy resin thickened with AEROSIL® 300 about 17 times. On the other hand the viscosity of epoxy resins thickened with hydrophobic grades AEROSIL® R 202 and AEROSIL® R 805 increases only slightly. The observed viscosity increase is a function of the addition of the silane. It is known for a long time that a minor addition of a bi-functional additive distinctly increases the thickening effect of fumed silica (13).

Figure 16 Comparison of viscosity changes of an epoxy resin (EPIKOTE 216) thickened with various AEROSIL® fumed silica grades as function of storage time at 50 °C.
Left: without silane addition
Right: with Gamma-glycidoxypropyl-trimethoxy-silane, DYNASYLAN® GLYMO



This additive effect is also observed in this system. Because hydrophilic AEROSIL® grades have a higher silanol group density than hydrophobic grades, the additive effect with AEROSIL® 300 is strongest. As seen in **Figure 17**, the storage time of 90 days at 50 °C has a strong influence on rheology of the thickened epoxy resin samples. After 7 days there appears a marked decrease of viscosity with the sample thickened with AEROSIL® 300. This decrease of viscosity continues to about 3 weeks. Then the measured viscosities remain constant to the end of the testing period. Both Figures show further that the measured viscosities of epoxy resins which were thickened with AEROSIL® R 202 and AEROSIL® R 805 remain almost constant during the storage time. Again the epoxy resin thickened with AEROSIL® R 805 shows the best storage stability (14).

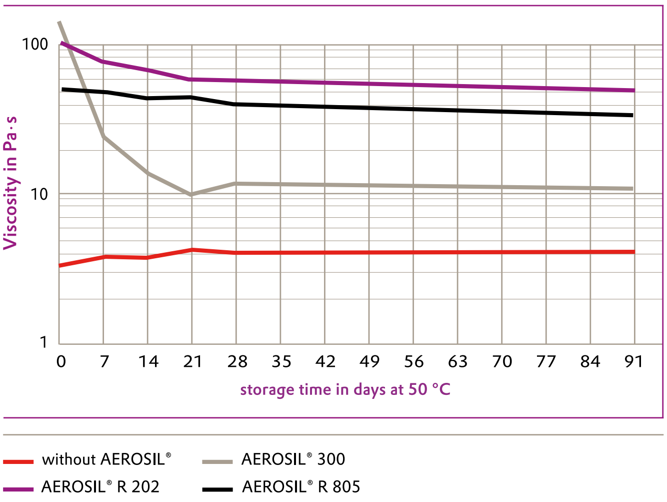
The distinct decrease of viscosity of samples thickened with AEROSIL® 300 can be traced to the reaction between Si-OH-groups of silica and the methoxy groups of the silane. With the reaction between silica and silane, the polar "additive" methanol is released. An increase in the level of polar additives lowers the thickening effect.

The good storage stability of the sample thickened with AEROSIL® R 805 can be attributed to the fact that this silica was hydrophobized with a silane and thus is no longer capable of a further reaction with silane.

2.4.3 AEROSIL® fumed silica as anti-settling agent in epoxy resins

In numerous solvent free epoxy resin systems fillers are being used. The reasons for this include improvement of thermo-mechanical properties, reduced shrinkage during hardening or economic considerations. Synthetic and natural fillers usually have particle sizes of 0.5–500 µm and possess densities of 2–4 g/cm³. They are more likely to settle.

Figure 17 Viscosity vs. time curves of 100 parts EPIKOTE 216 with 2 parts silane and 4 parts of various AEROSIL® fumed silica grades at 50 °C



AEROSIL® fumed silica can prevent or at least slow down the settling of fillers or pigments in heavily loaded systems. After long storage times, some settling may be observed however in many cases with AEROSIL® fumed silica sedimentation is soft and can be easily resuspended. This effect is mainly due to the reduced mobility of the pigments/fillers in the liquid system and mainly caused by a yield-value and less on the viscosity increase (**Figure 18**).

The AEROSIL® fumed silica epoxy resin system discussed in **Figure 17** was additionally mixed with 20 parts of treated calcium carbonate and submitted to the same test conditions (**Figure 19**). The hydrophobic AEROSIL® types R 202 and R 805 hold the calcium carbonate in suspension after 90 days of storage time at 50 °C. The most storage stable system in this comparison is achieved by use of AEROSIL® R 805. The test with the hydrophilic silica AEROSIL® 300 and 20 parts chalk shows after 28 days of storage time a sedimentation of fillers, so that the measurement of viscosity could only be conducted during the first 4 weeks of storage time.

Figure 18 Yield values of EPIKOTE 216 with 2 parts of various AEROSIL® fumed silica grades at room temperature

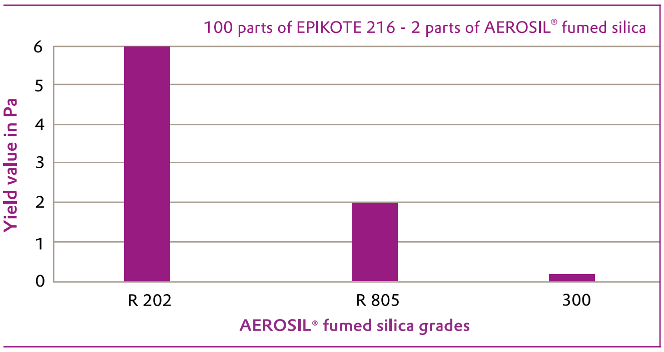
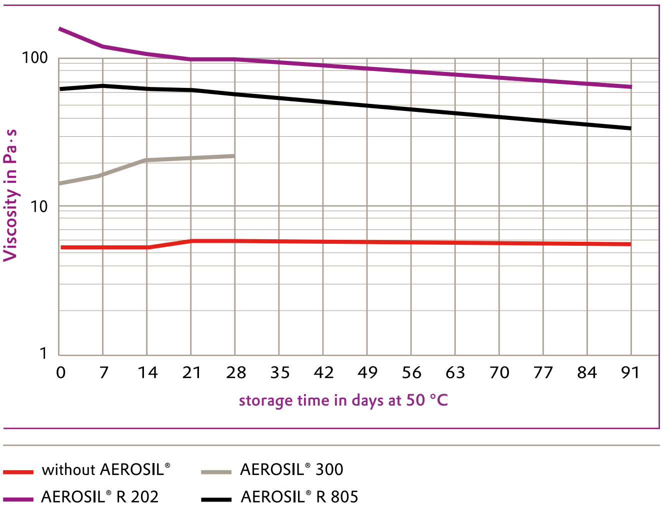


Figure 19 Viscosity curves of 100 parts EPIKOTE 216 with 2 parts silane, 20 parts of chalk and 4 parts of various AEROSIL® fumed silica grades at 50 °C



2.4.4 Thickening and thixotropy of hardeners for epoxy resins

To obtain the final properties of epoxy resin formulations, the composition of the mixture of the resin and hardener must be checked during the process. It is important that both parts are mixed homogeneously. Due to the hardener being generally lower in viscosity than the epoxy resin, blending mistakes can easily occur during the processing. The final properties of the cured epoxy resin formulations are negatively influenced due to both parts not being mixed well.

By adding thickening and thixotropy to the hardener these blending mistakes can be avoided. In many cases with the addition of silica to both sides the processing is improved whereby an inhomogeneous blending is avoided.

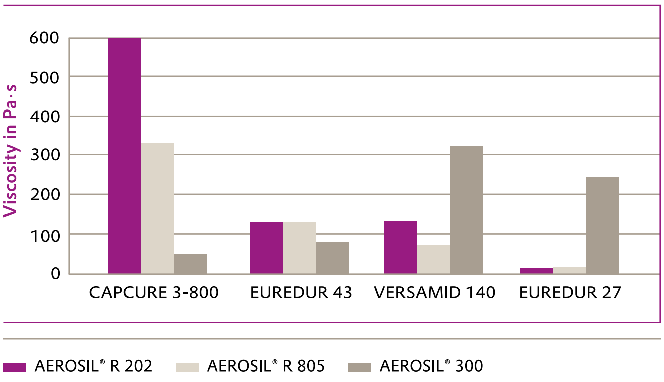
Beyond that also fillers can be added to the hardener components. This requires the addition of fumed silica as an antisettling agent.

An example for the multitude of epoxy resin hardeners shown in **Figure 20** is the thickening effect of silica AEROSIL® R 202, AEROSIL® R 805 and AEROSIL® 300 with four different hardeners.

In relatively non-polar polyaminoamide (VERSAMID 140) and etherdiamine (EUREDUR 27), AEROSIL® 300 is the most effective thickening agent. In high-polar mercaptan hardeners (CAPCURE 3-800), hydrophobic types AEROSIL® R 202 and AEROSIL® R 805 are very effective. In the partly-polar cycloaliphatic polyamine (EUREDUR 43), the hydrophilic and hydrophobic AEROSIL® fumed silica grades have a similar thickening effect (14).

The influences of functional silanes on the rheology of silica containing hardeners are essentially the same as with epoxy resins. Also with hardeners for epoxy resins, the hydrophobic types show a very good storage stability while the rheological properties can change with time when hydrophilic silica are used.

Figure 20 Thickening of various epoxy hardeners with AEROSIL® 300, AEROSIL® R 202 and AEROSIL® R 805 at room temperatures

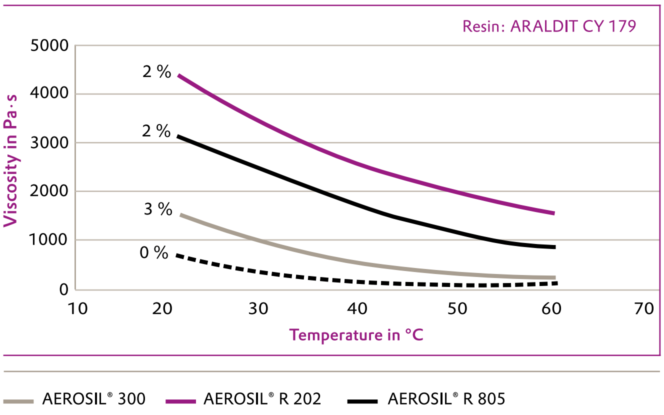


2.4.5 Temperature influence

With increasing temperature, the viscosity of epoxy resin systems decreases. In formulations which were thickened with AEROSIL® fumed silica, viscosity also decreases. Because of the higher adjusted viscosity the remaining viscosity is still sufficient to warrant a perfect processing of the resin.

In **Figure 21** the dependency on temperature of viscosity of a hot-curing epoxy resin (ARALDIT CY 179) with and without AEROSIL® fumed silica can be seen. AEROSIL® R 202 acts most favorably, followed by AEROSIL® R 805 (15).

Figure 21 Viscosity of ARALDIT CY 179 with different AEROSIL® fumed silica grades depending on the temperature. Concentration 2 % and 3 % (18)



2.4.6 Rheological characteristics of epoxy resin formulations containing silica during the curing process

The rheological characteristics of epoxy resin formulations during the curing process are of special interest to the processor. Thixotropy, viscosity and yield-value must remain stable during potlife in order to prevent sagging on vertical surfaces as well as sedimentation of fillers.

The hardeners mostly used in practice are amine hardeners. They, as a rule, can be thickened with hydrophilic AEROSIL® fumed silica grades, as was already shown in the previous section. The viscosity increases significantly after the addition of an amine hardener to a thixed epoxy resin, compared to a pure thixed epoxy resin without hardener. In the course of the potlife new polar hydroxyl groups are formed so that AEROSIL® 300 loses some rheological efficiency (solvating effect) and thixotropy, viscosity and yield value decrease.

This effect can be demonstrated both by:

- simple sagging tests (**Figure 22**)
- by measuring viscosity during the hardening with the Brookfield-Viscometer (**Figure 23**, **24**)
- or by measuring the rheological properties with a cone and plate rheometer (**Figure 25**).

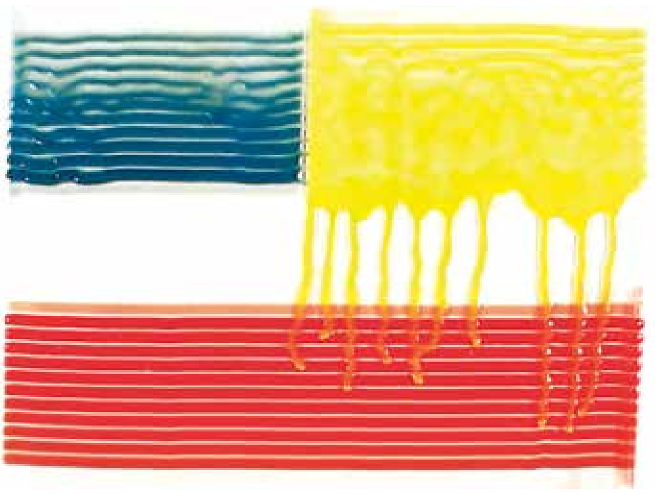


Figure 22
Sagging behavior of a 2-component epoxy resin, shown on a vertically standing glass plate after about one hour.

red:	4 % AEROSIL® R 202
blue:	4 % AEROSIL® R 805
yellow:	4 % AEROSIL® 300

Figure 23 and **24** show two other epoxy/amine hardening systems with variable potlifes. The viscosities were measured here with the Brookfield viscometer at 2.5 rpm after addition of the non-thixed hardener until just before the gelling time.

This measurement on this low shear-rate corresponds to the shear during sagging. These measurements also confirm the results shown already in **Figure 8**. During the hardening process a large decrease of the initial viscosity is noted with those systems thixed with AEROSIL® 300, while none or only a slight decrease of the initial viscosity appears with systems containing AEROSIL® R 202 and AEROSIL® R 805. The same results are listed in the following resins/hardener systems, as they are also already discussed in the fourth edition of this Series Technical Bulletin Pigments number 27.

Figure 23 Viscosity curves of a 2-component epoxy resin (potlife 45 min.) with 4 % AEROSIL® fumed silica during curing (EUREPOX 730 and EUREDUR 250/13).

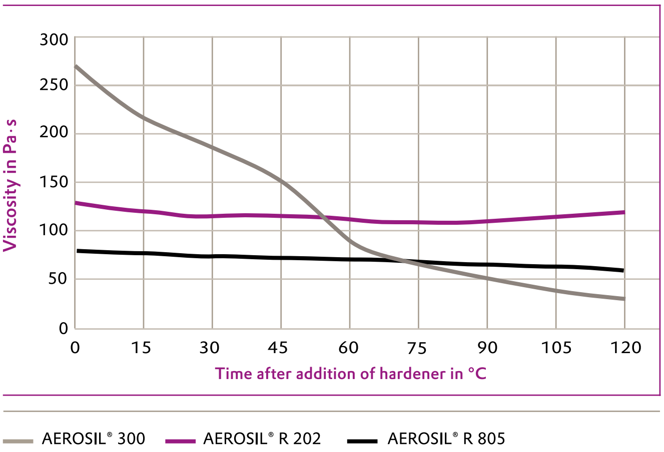
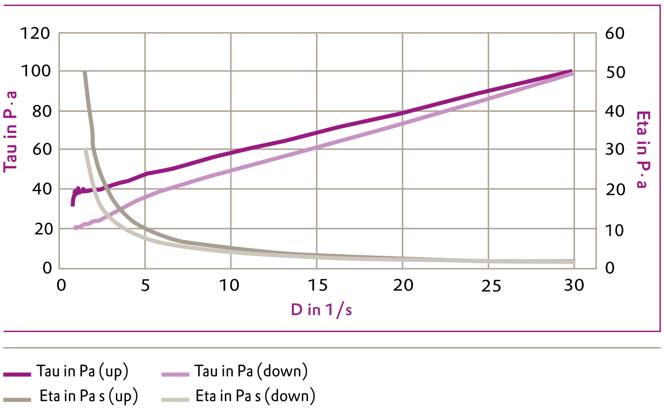


Figure 24 Viscosity curves of a 2-component epoxy resin (potlife 120 min) with 4 % AEROSIL® fumed silica during curing (EUREPOX 776 and VERSAMID 145)

The epoxy resin, which was thixed with the hydrophobic AEROSIL® fumed silica grade AEROSIL® R 202 shows a certain thinning effect after the addition of the amine hardener (see **Figure 8**). The change of polarity of the resin mixture during the curing barely influences the very good rheological properties. Thixotropy, yield-value and viscosity remain constant during the potlife, so that the epoxy resin mixture will not sag on vertical surfaces (**Figure 25**). Similar results are obtained when using AEROSIL® R 805.

Figure 25 Viscosity and flow curves of an epoxy resin thixed with AEROSIL® R 202, 27 min. after addition of the hardener



2.5 AEROSIL® fumed silica as free-flow agent

In powders AEROSIL® fumed silica acts as a free-flow aid and prevents clumping during storage. The mechanisms of action are varied. The AEROSIL® fumed silica particles can encase the subtantially larger powder particles and thus prevent contacts, which i.e., can lead to the formation of sinter bridges. Also, the adsorption of moisture which can build up fluid bridges is possible. In this case, AEROSIL® fumed silica particles can be regarded as a spacer, which minimize the forces of attraction. If moisture is responsible for the clumping of a powder, the best results can be obtained with hydrophobic AEROSIL®. In epoxy resin powders, AEROSIL® R 972 has proven itself a free flow aid. In contrast to the negative charge impacted by AEROSIL® fumed silica, AEROXIDE® Alu C inputs a positive charge in some powder coatings. This positive charge not only helps to improve free flow but helps to improve application during the deposition process.

Table 3 shows cone heights (freeflow test) and the electrostatic charge of two commercially available epoxy based coatings without and with various amounts of AEROSIL® R 972. AEROSIL® R 972 was added to the powder coatings after pulverization. In practice it may be more advantageous to add AEROSIL® R 972 – or also AEROXIDE® Alu C – before pulverization.

Table 3 Cone heights and electrostatic charge of two commercially available powder coatings without and with an AEROSIL® R 972-additive (18)

	Powder coating			
	R 2433		**R 2519**	
	Free flow cone height mm	Electro static charge V/cm	Free flow cone height mm	Electro static charge V/cm
Without addition	38	+460	26	−40
+ 0.1 % AEROSIL® R 972	32	+120	18	−40
+ 0.2% AEROSIL® R 972	24	+50	18	−30
+ 0.3% AEROSIL® R 972	22	+40	–	–
+ 0.4% AEROSIL® R 972	22	+50	18	−20
+ 0.5% AEROSIL® R 972	24	+90	–	–
+ 0.6% AEROSIL® R 972	–	–	18	−20

3 Summary

The experiments described in this brochure show that AEROSIL® R 202 and AEROSIL® R 805 are excellent thixotropes for liquid epoxy resins. Although AEROSIL® R 202 is rheologically more effective, AEROSIL® R 805 should always be considered especially in cases when adhesion and leveling are adversely influenced by AEROSIL® R 202.

In addition AEROSIL® R 805 used in bisphenol A-systems shows even better storage stabilities than with AEROSIL® R 202. The previously mentioned facts do not exclude that in some systems satisfactory results can be obtained also with AEROSIL® 300 or AEROSIL® COK 84.

For the enhancement of flow and electrostatic chargeability of powder coatings AEROSIL® R 972 and AEROXIDE® Alu C are recommended.

Table 4 gives a general view of the possible applications of AEROSIL® fumed silica in epoxy resins.

Table 4 Possible application of AEROSIL® fumed silica in epoxy resins

	Thickening and thixotropy	Anti settling agent	Free-flow aid
Coating resins	●	●	
Powder coatings	●		●
Casting resins	●	●	
Impregnating resins	●		
Adhesives	●		
Laminating resins	●	●	
Patching compound resins	●	●	
Dip-coating resins	●	●	

4 Physiological behavior and workers safety

Because of its X-ray amorphous structure, AEROSIL® fumed silica causes no silicosis. In employees in these manufacturing plants who in part come in contact for decades with these substances and are subject to strict medical supervision pervision, no sort of symptoms of silicosis were found. Also numerous studies of inhalations using animals remained incident free.

A few physiological effects of AEROSIL® ON HUMANS AND ANIMALS are summarized in **Table 5**.

Table 5

Oral Intake humans	**without finding**
Intact human skin	**without finding**
Inhalation–humans	**no silicosis**
Inhalation–rat	**no silicosis**
LD_{50}, rat	**10 g/kg**
Mucous membrane rabbit eye	**without finding**
Scarified rabbit skin	**without finding**
Intact rabbit skin	**without finding**

Orally taken, AEROSIL® fumed silica passes the stomach-intestine tract without being resorbed in traceable amounts.

Also on the skin AEROSIL® fumed silica is harmless. It can –on occasion– produce a feeling of which can easily be removed by washing and normal skin care.

The MAK-value for pyrogenic silica lies in the Federal Republic of Germany at 4 mg/m^3 total dust at an evaluation time of 8 hours. In the edition No. 28 of the Technical Bulletin Fine Particles all questions of handling of synthetic silicas are discussed, among them also technical possibilities which can secure the observance of a determined MAK-value.

5 Literature

(1) Technical Overview, AEROSIL® Fumed Silica

(2) AEROSIL® Product Overview, Evonik Industries AG

(3) „Quality for the Surface Protection", brochure of the firm Schering AG, D-59192 Bergkamen (1989)

(4) F. Lohse in: BECKER/BRAUN, Plastics Handbook, vol. 10., Hanser Publishers, D-81679 München (1988)

(5) „Cold curing Epoxy-thermosets", brochure of the firm Dow Chemical Rheinwerk GmbH, D-77836 Rheinmunster (1987)

(6) J. Möckel, Kunststoffe 80,1177 (1990)

(7) Farbe + Lack 98, 61 (1991)

(8) G. Schramm, Introduction to Practical Viscosimetry, Haake Messtechnik GmbH & Co., D-76227 Karlsruhe (1987)

(9) M. H. Pahl, H. M. Laun, W. Gleissle, Practical Rheology of Rastics and Elastomers, VDI, D-40239 Dusseldorf (1989)

(10) H. Ferch in H. Kittel, Textbook of Varnishes and coatings, volume 2, W. A. Colomb Publishers, D-1000 Berlin (1974)

(11) M. Zlokarnik in ,,Ullmanns Encyclopedia of Industrial Chemistry" volume B2, VCH Publishing Company, D-69469 Weinheim (1988)

(12) H.-P. Wilke: Stirring Technique, Chemical Engineering and Apparative Fundamentals, Huthig Publishers, D-69121 Heidelberg (1991)

(13) R. Bode, H. Ferch, H. Fratzscher, Kautschuk + Gummi Kunststoffe 20, 578 (1967)

(14) M. Jarmer: Rheological Properties of Fumed Silicas in EP Resins", unpublished lecture, Chemspec USA 90 Symposium, Philadelphia, USA, (1990).

(15) Technical Bulletin Fine Particles No. 27, AEROSIL® fumed silica for solvent-free epoxy resins, Evonik Industries AG

6 Physico-chemical data of AEROSIL® fumed silica and AEROXIDE® Alu C

Characteristic physical and chemical data of AEROSIL® fumed silica

Test methods	AEROSIL® 300	AEROSIL® COK 84	AEROSIL® R 202	AEROSIL® R 805	AEROSIL® R 812	AEROSIL® R 812 S	AEROSIL® R 972	AEROSIL® R 974	AEROXIDE® Alu C
CAS-Reg. Number	112945-52-5 (formaly: 7631-86-9)	112945-52-5/ 1344-28-1	67762-90-7	92797-60-9	68909-20-6		60842-32-2 (formaly: 68611-44-9)		1344-28-1
Behaviour towards water	hydrophilic		hydrophobic						hydrophilic
Appearance	-fluffy white powder -								
BET surface area BET[1] m²/g	270–330	155–215	80–120	125–175	230–290	190–245	90–130	150–190	85–115
Tapped density[2] approx. value									
Standard material g/L	50	50	60	60	60	60	50	50	50
Densified material (suffix „V“) g/l	120	–	–	–	–	–	90	90	–
Densified material (suffix „VV“) g/l	50/75/120[17]	–	60/90[18]	60/90[18]	60/90[18]	60/90[18]	–	–	–
Loss on drying[3] wt. % (2 h at 105 °C) when leaving the plant	≤1.5	≤1.5	≤0.5	≤0.5	≤0.5	≤ 0,5	≤ 0.5	≤ 0.5	≤ 5
Loss on ignition[4, 7] wt. % (2 h at 1000 °C)	≤2	≤1	4–6[12]	5–7[16]	1.0–2.5[13]	≤ 1.5–3.5[14]	≤2[11]	≤2[15]	≤3
C-content wt. %	–	–	3.5–5.0	4.5–6.5	2.0–3.0	3.0–4.0	0.7–1.0	0.8–1.4	–
pH-value[5] (4% aqueous dispersion)	3.7–4.5	3.6–4.3	4–6[9]	3.5–5.5[9]	5.5–7.5[9]	5.5–7.5[9]	4.0–5.5[9]	3.8–5.0[9]	4.5–5.5
SiO_2[8] wt. %	≥99.8	82-86	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≤0.1
Al_2O_3[8] wt. %	≤0.03	14-18	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≥99.6
Fe_2O_3[8] wt. %	≤0.003	≤0.1	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.01	≤0.2
TiO_2[8] wt. %	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.03	≤0.1
HCl[8, 10] wt. %	≤0.025	≤0.1	≤0.025	≤0.025	≤0.025	≤0.025	≤0.05	≤0.05	≤0.5
Sieve residue[6] (by Mocker, 45 µm)	≤0.025	≤0.1	–	–	–	–	–	–	≤0.05
Unit weight[17] (netto) kg	10	10	10	10	10	10	10	10	10

The data have no binding force.

---

[1] accord. to DIN EN ISO 66131
[2] accord. to DIN EN ISO 787-11, JIS K 5101/18 (not sieved)
[3] accord. to DIN EN ISO 787-2, ASTM D 280, JIS K 5101/21
[4] accord. to DIN EN ISO 3262-20, ASTM D 1208, JIS K 5101/23
[5] accord. to DIN EN ISO 787-9, ASTM D 1208, JIS K 5101/24
[6] accord. 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] in water: ethanol 1:1
[10] HCl-content is a part of the ignition loss
[11] contains approx. 0.6–1.2 % chemically bound carbon
[12] contains approx. 3.5–5.0 % chemically bound carbon
[13] contains approx. 2.0–3.0 % chemically bound carbon
[14] contains approx. 3.0–4.0 % chemically bound carbon
[15] contains approx. 0.7–1.3 % chemically bound carbon
[16] contains approx. 4.5–6.5 % chemically bound carbon
[17] packaging of densed material: 20 kg
[18] packaging of densed material: 15 kg

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